
***Strain rate sensitivity of polycarbonate and vinyl ester from
dynamic mechanical analysis experiments***

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ABSTRACT

Measuring the strain rate sensitivity of materials is desired to improve the design of polymeric parts in automotive and aerospace structures. In this work, we present a technique for determining the mechanical response of polymers at different temperatures and strain rates by converting frequency-domain dynamic mechanical analysis (DMA) data to the time domain.

Two polymers of practical interest, vinyl ester and polycarbonate, are examined. The modulus of elasticity in the linear region is measured as a function of the applied strain rate, and compared to predictions from the DMA transformation technique. Close agreement between the results obtained from the two techniques is observed over the studied range of strain rates. The transformation technique only relies on the assumptions of the linear theory of viscoelasticity and is expected to be applicable to a wide range of polymers and can also be extended to polymer-matrix composites.

Keywords: Strain rate, viscoelasticity, dynamic mechanical analysis, vinyl ester, polycarbonate

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INTRODUCTION

Dynamic mechanical analysis (DMA) is a widely-used technique in polymer science for determining thermal properties of materials, such as polymeric solids [1-3] and complex fluids [4]. The technique involves applying an oscillatory deformation to a specimen and measuring the resulting stresses. The measured stress is divided by the maximum strain, and the in-phase and quadrature components of the response are termed the storage modulus E' and the loss modulus E'' , respectively. These quantities are measured as functions of temperature or loading frequency and can be used to determine a number of important parameters and qualitative assessments [5]. The most fundamental result is computation of the transition temperatures, such as the glass transition temperature T_g , for which DMA is considered by far the most accurate technique [6]. These transitions have numerous interpretations, such as in determining activation of chain dynamics [7-9], the miscibility of polymer blends [10, 11], and studying polymer crystallization [12]. Such measurements have various practical uses in formulating and blending polymer mixtures [13-15].

Despite the large amount of information about the dynamic response of materials they contain, DMA results have rarely been applied to design and engineering of structures subjected to dynamic loading. This is because the frequency and temperature dependent information obtained from the experiments is not directly or trivially applicable to design problems. Often, the domain over which certain approximations are valid is small, leading to inaccurate predictions. There is also difficulty in converting from frequency to a nominal strain rate, and assuming the storage modulus at that frequency to be equivalent to the Young's modulus at some strain rate [16]. This can be interpreted as attempting to find an analogy to the empirical Cox-Merz rule from

rheology, which works well for complex fluids including blood [4, 17]. However, the relaxation process in fluid flow is not the same as in deformation of a solid, therefore, a different approach is used in the present work. The determination of the strain rate sensitive Young's modulus involves use of an integral transform to convert the frequency domain results to time domain, and a convolution type integral to obtain a stress-strain relationship. Other interconversions have been utilized, usually to determine the relaxation spectrum [18, 19], which is not as readily useful in computing time domain response. These interconversions also have applications in the interpretation of dielectric data [20] as they are mathematically very similar.

Previous works on correlating DMA results to elastic constants at various strain rates have matched the measured transitions with the results of a carefully controlled small set of experiments. However, these studies have not extended to offering useful predictions outside the measured range. For instance, critical strain rates at which the material's rate sensitivity changes are related to the thermal transitions measured in DMA [21]. In this work, we utilize the linear theory of viscoelasticity to convert the results from DMA into a time-domain relaxation function, which is used to directly find the strain rate sensitive mechanical behavior of the material [22] and which can also be used in finite element analysis for complex loading scenarios [1]. In order to characterize the master curve over a sufficiently wide range of frequencies to ensure convergence of the transform to the correct relaxation function, the time temperature superposition (TTS) principle [23] is used to extend the frequency domain results over a substantially wider range by shifting experiments at different temperatures to form a master curve. This master curve is fitted to a physically motivated model function, and the integral transform is computed numerically as a convergent alternating sequence. The time-domain

relaxation function is used to determine the strain rate sensitivity of two common engineering polymers, vinyl ester and polycarbonate, a thermoset and a thermoplastic polymer, respectively. The results are compared to a separate set of tension tests conducted at a range of strain rates. Close agreement is found between the DMA predictions and the results from the tension tests.

The results of this work are expected to be highly useful to the composites community. In most composite materials, the primary source of strain rate sensitivity is the matrix resin [24], so quantification of this sensitivity can help in identifying the critical frequencies or strain rates where the effective material properties will change. Mathematical models are also available that predict the frequency sensitivity of composites from a micro-mechanics approach [25-27], and the methods of this work can be used to convert the predicted frequency sensitivity into the strain rate sensitive mechanical properties.

MATERIALS & METHODS

Materials

Polycarbonate (PC) sheets of nominal dimensions $45 \times 30 \times 0.328 \text{ cm}^3$ were procured from Canal Plastic Center, New York, NY. US Composites 700 vinyl ester (VE) resin was catalyzed at 1% (by volume) with methyl ethyl ketone peroxide (MEKP). The vinyl ester was fabricated by casting in aluminum molds and curing at room temperature for 24 hours and at $90 \text{ }^\circ\text{C}$ for 1 hour. Rectangular specimens of nominal dimensions $135 \times 6.35 \times 3.2 \text{ mm}^3$ were machined for tensile testing and of $35 \times 11.64 \times 2.84 \text{ mm}^3$ were machined for DMA. Othermill Pro CNC (Other Machine Co, Berkeley, CA, USA) was used to machine both tensile and DMA bars.

Dynamic mechanical analysis

TA Instruments (New Castle, DE, USA) Q800 was used in the single cantilever bending configuration with a span length of 17.5 mm. Temperature sweeps were conducted at 1°C/min from -100°C to 150°C for PC and at 2°C/min from -100°C to 170°C for VE at constant frequency of 1Hz. Frequency sweeps are conducted at steps of 5°C from -30°C to 80°C for PC and -10°C to 140°C for VE, with 8 minutes of soaking time at each step before sweeping at 20 logarithmically spaced frequencies in the range 1-100Hz.

Tensile testing

An Instron 4467 universal testing system (Instron, Norwood, MA, USA) was used for tension testing. Tests are conducted at various strain rates in the range 10^{-6} - 10^{-2} s⁻¹ up to failure or 5% strain, whichever occurred first. An extensometer of 1 in gage length was used for displacement measurement.

RESULTS AND DISCUSSION

Results of the temperature sweeps on PC and VE are shown in Figure 1. VE has a glass transition at around 120 °C and a β -transition at around -75 °C. The glass transition and the β -transition temperatures of PC are not well resolved in the test temperature range in this work. The storage modulus decreases monotonically with increasing temperature as these polymers do not exhibit entropic elasticity. Representative frequency sweep results for PC and VE are shown in Figure 2. For both materials, storage modulus increases with increasing frequency and decreases with increasing temperature. The TTS principle is applied by shifting the frequency sweep curves along the frequency axis to form a master curve [28], shown in Figure 3. The resulting master curve represents the storage modulus at the reference temperature but extended

over a significantly wider range of frequencies than accessible by the machine directly.

However, this data still represents the steady state harmonic response, requiring the use of the transform procedure below to convert to an effective elastic modulus at different strain rates. The shift factors used to create the E' master curves are also used to shift the E'' data. The ability to form master curves for both complex modulus components using the same shift factors is one indication of thermorheological simplicity [29], and that the TTS principle applies. Tensile test results at different strain rates presented in Figure 4 show strain rate sensitivity in the tensile modulus.

In order to use the DMA results to predict the tensile response, the material function characterized by the frequency master curve must be converted into a time domain relaxation function $E(t)$. From the linear theory of viscoelasticity, the conversion takes the form of a Fourier sine transform [30]

$$E(t) = \frac{2}{\pi} \int_0^{\infty} \frac{E'(\omega)}{\omega} \sin(\omega t) d\omega \quad (1)$$

where ω and t are the angular frequency and time, respectively. As this integral covers the positive real half line, the data must be extrapolated over this range. To do so, the storage modulus master curve at the desired reference temperature is fitted to a combination of sigmoidal functions of $\log(\omega)$. A general expression for such a fit function is

$$E'(\omega) = c_1 + \sum_{j=1}^N c_{j1} \tanh(c_{j2} \log(\omega) + c_{j3}) \quad (2)$$

where the c 's are fitting coefficients and $\log(\omega)$ is the natural logarithm. Use of this function implies that there are N smooth step transitions in the storage modulus curve and N peaks in E'' , and that the behavior is bounded at zero or $+\infty$ frequency. N is chosen by examining the number

of peaks in the E'' master curve, as it is difficult to distinguish multiple step transitions from the E' master curve. This form provides a more compact representation of the storage modulus function than the Prony series model because each relaxation process (or transition) requires only three extra coefficients, while a large number of exponential functions are required to model each relaxation in the Prony representation. However, this function is not guaranteed to satisfy the nonnegative requirement that results from thermodynamics [31] unless $c_1 \geq \sum c_{j1}$.

In the PC master curve, evidence of two peaks is observed. Neither peak is fully captured due to the limited temperature range feasible for performing temperature sweeps. In VE, two peaks are captured. Based on these observations $N = 2$ is chosen for fitting of both master curves. Previous work on HDPE observed a single peak in the master curve, which leads to a simple sigmoidal equation for which analytical manipulation is trivial [32]. In that case, it is straightforward to apply approximate interrelationships and find transition frequencies and properties of the transition from the fit coefficients. In the general N -transition case there is no simple closed form solution, and numerical solution is needed (but trivially simple).

The R^2 value of the curve fit to the master curves is above 0.99 for both materials, indicating an appropriate fit. For PC, the zero-frequency asymptote is around 900 MPa, while for VE the nonnegativity condition is violated and the asymptote is around -600 MPa. However, the crossover to negative storage modulus occurs at around 3×10^{-18} Hz, which is sufficiently small that it has insignificant impact on the computation of $E(t)$. The resulting relaxation functions are shown in Figure 5, and can be observed to satisfy the requirements of fading memory and nonnegative stored and dissipated energy [31]. These requirements can be expressed as

$$E(t) \geq 0, \quad dE(t) \leq 0, \quad d^2E(t)/dt^2 \geq 0. \quad (2)$$

The relaxation function is convolved with a strain history function to calculate the stress as a function of time [30]:

$$\sigma(t) = E \times d\varepsilon = \int_{-\infty}^t E(t-\tau) \frac{d\varepsilon(\tau)}{d\tau} d\tau \quad (3)$$

where σ , ε , and τ represent stress, strain and the time variable used for integration, respectively.

In a standard tension test, the idealized deformation history has a strain rate of $\dot{\varepsilon}$ beginning at $t = 0$. Substituting this strain history function into Equation 3, the convolution becomes

$$\sigma(t) = \dot{\varepsilon} \int_0^t E(\tau) d\tau \quad (4)$$

From the stress-strain curve that results, various properties of interest can be calculated. The modulus is estimated by evaluating the secant modulus at 0.5% strain, since the elastic region for viscoelastic materials is usually not linear. The predictions of the secant modulus are compared against the tensile experiments in Figure 6. In addition, values from the literature for vinyl ester at higher strain rates [33] are shown on the same figure, and also agree well with the prediction. A recent study has proposed a method for determining the range of strain rates for which the predicted modulus obtained from tensile tests can be matched with the predictions obtained from transforming the DMA data from frequency- to time-domain. This work derived the limits on the strain rates for which such predictions would be valid from a given set of DMA data. [22].

Within this region, the prediction is determined primarily by the master curve rather than by the extrapolated curve. The presence of other transitions at other reduced frequencies that are not captured by experiments can cause inaccurate values of the modulus outside of the range. Using this prediction, the upper strain rate limit for the present work is about 10^9 s^{-1} for PC and 10^3 s^{-1} for VE. All of the experimental data available in the literature that report the strain rate sensitive

modulus is within these ranges, which shows the range of strain rates of interest for these polymers. The ability of the model to cover these strain rates for prediction is useful in engineering design.

CONCLUSIONS

In this work, a correlation is explored between the strain rate sensitive elastic properties and the dynamic mechanical properties of polymers. Using the time temperature superposition principle, the storage modulus is obtained for over 20 decades of frequency. A physically-motivated fitting function is used to extrapolate the storage modulus so that an integral transform can be computed, which converts the data to a time domain function. The time domain function is validated on a thermoplastic and a thermoset polymer by comparing with the results of separate tensile tests, and excellent agreement is observed over a wide range of strain rates. The relaxation function can be used in finite element simulations to determine the response to complex loading scenarios, such as the nonsteady pulse used in many high strain rate methods, or for complex geometry.

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Figure Captions

Figure 1. Storage and loss modulus temperature sweeps at 1 Hz for (a) polycarbonate and (b) vinyl ester.

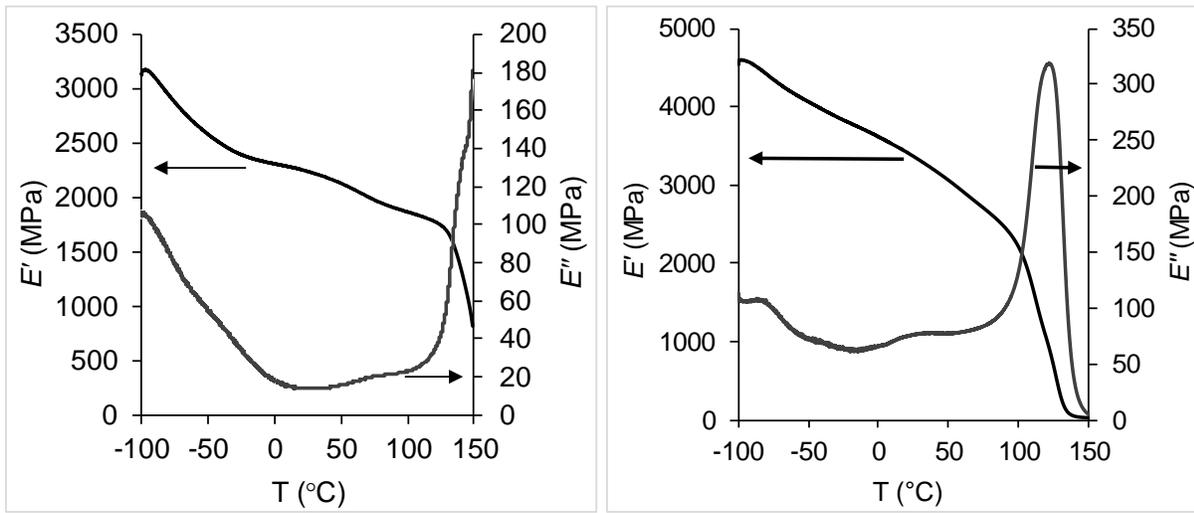
Figure 2. Storage modulus frequency sweeps for (a) polycarbonate and (b) vinyl ester.

Figure 3. Master curves for storage and loss modulus at 20 °C for (a) PC and (b) VE.

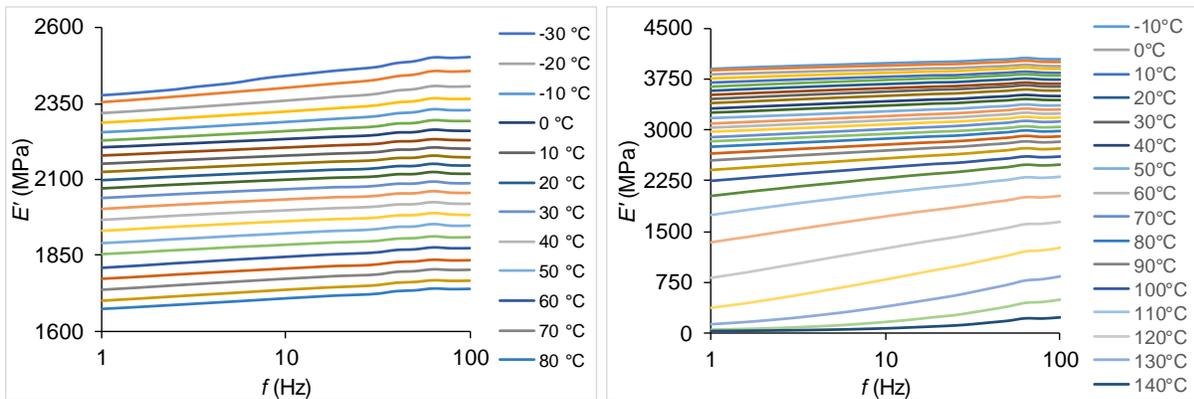
Figure 4. Tensile stress-strain curves at different strain rates for (a) polycarbonate and (b) vinyl ester.

Figure 5. Relaxation functions obtained by numerically integrating the transform in Equation (2).

Figure 6. Comparison of secant modulus predictions from the DMA transform with values from separate tensile testing and literature values [33].



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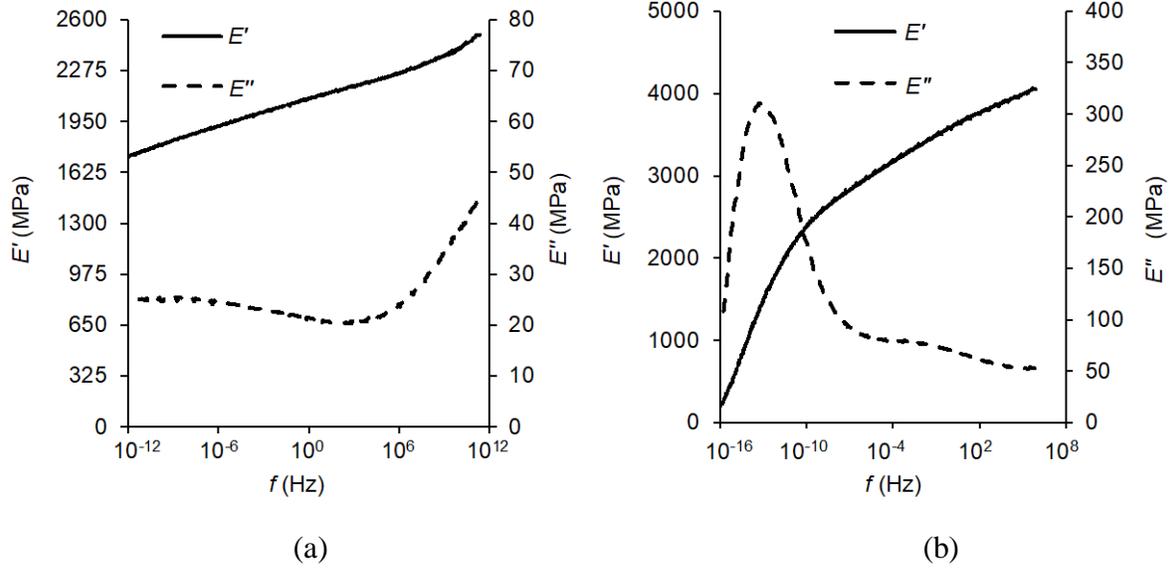


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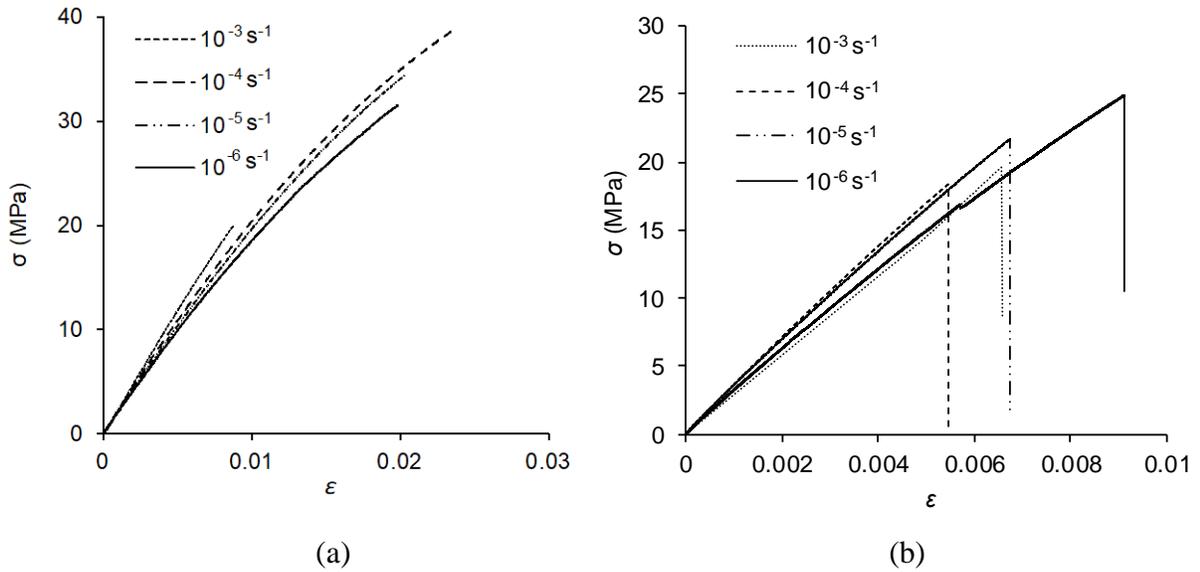


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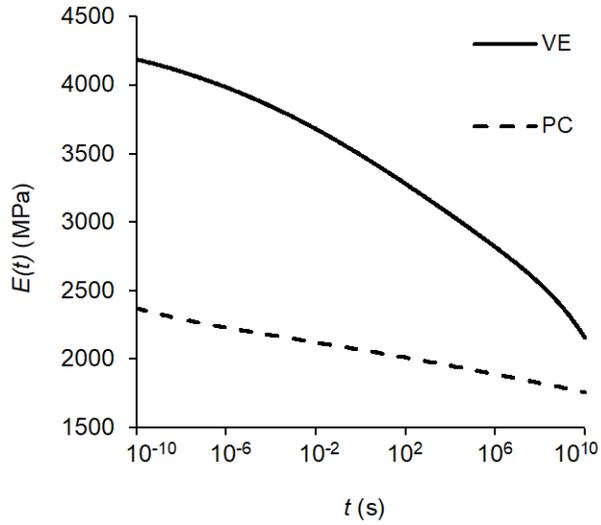


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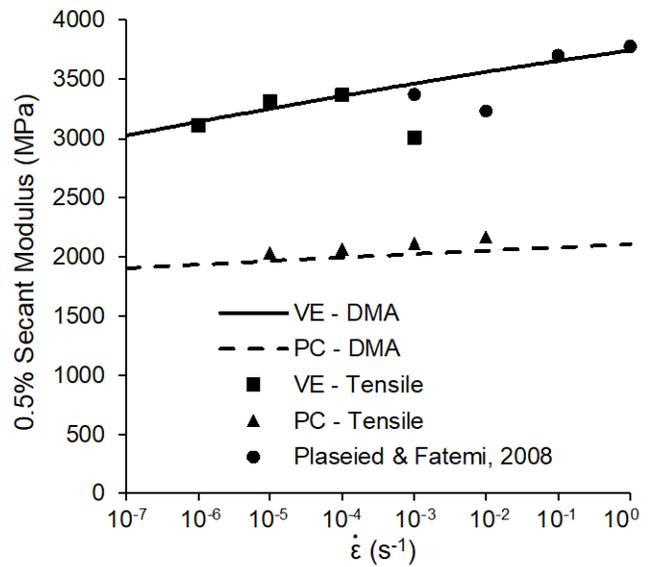


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