

PREDICTION OF STRAIN RATE SENSITIVITY OF POLYMERS BY INTEGRAL TRANSFORM OF DMA DATA

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ABSTRACT

Interest in designing lightweight structures has resulted in the adoption of polymers and particulate composites in numerous structural applications. Weight saving is extremely beneficial both in terms of increased payload and reduced fuel consumption in transportation sector. Major challenges to the adoption of composite materials for such applications include unavailability of predictive models for high strain rate response and creep life. Dynamic mechanical analysis (DMA) is a widely used technique in polymer science for determining transition temperatures and activation energies. However, DMA results are not directly applicable to the design of structures because only frequency-domain properties are reported from those measurements. This work develops a transformation method for converting the DMA data from frequency to the time domain by appropriate integral relations from viscoelasticity theory. The material relaxation function can then be determined in order to predict the response over varying strain rates and loading conditions. The procedure is demonstrated for three material systems: vinyl ester, polycarbonate and high density polyethylene/fly ash composites. Close matching between the DMA predictions and the results of separate tensile tests and literature data is observed at a wide range of strain rates.

1 INTRODUCTION

Dynamic mechanical analysis (DMA) is a widely-used technique in polymer science for determining thermal properties of materials. It is primarily applied to solid polymers [1-3], but is also applicable for the shear properties of complex fluids [4, 5]. A dynamic mechanical analyzer applies an oscillatory deformation to the material and measures the resulting stress as a function of time. Due to the viscoelastic response of the material, there is a phase lag between the stress and strain in steady state oscillation. The in-phase and quadrature (90° out of phase) components of the response are termed the storage modulus E' and the loss modulus E'' , respectively. The phase angle δ is not reported directly, but rather given as the tangent of the angle, $\tan(\delta)$. These quantities are measured as functions of temperature or loading frequency and are then analyzed to determine various thermal properties of the material [6]. The most common use of DMA is to find the transition temperatures in amorphous materials, such as the glass transition temperature T_g . DMA is considered by far the most accurate technique [7], with perhaps an order of magnitude greater accuracy as compared to differential scanning calorimetry. These transitions reveal activation of different degrees of freedom in the chain dynamics [8-10], which can be further bolstered with spectroscopy methods such as nuclear magnetic resonance to determine which side groups are freed in each transition. Analysis of the shape of the transition also gives information about the miscibility of polymer blends [11, 12]. These characterizations have many practical uses in formulating and blending polymer mixtures [13-15] to ensure their compatibility and stability.

Despite containing a large amount of information about the dynamic response of materials, the data from DMA experiments rarely find use in design and engineering of structures. It is desired that a correlation be developed so that these data can be practically used in the modelling of structures subjected to dynamic loading. The difficulty in achieving this comes from the difficulty in converting

the frequency and temperature dependent information obtained from the experiments into time-domain representations that can be numerically or analytically computed. Simple approximations are available, but often the domain over which they are valid is small, leading to inaccurate predictions. For example, it is not possible to convert directly from frequency to a nominal strain rate and assume the storage modulus at that frequency to be equivalent to the Young's modulus at some strain rate [16]. The proper determination of the strain rate sensitive Young's modulus involves the use of an integral transform to convert the frequency domain results to time domain and a Stieltjes convolution integral to obtain a stress-strain relationship.

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 rate sensitivity changes, are related to the thermal transitions measured in DMA [17]. 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 response of the material [18] and which can also be used in finite element analysis for complex loading scenarios.

The method described in this work makes use of the time-temperature superposition (TTS) principle [19] to obtain the storage modulus over a wider range of frequencies than directly attainable by any single experimental technique. TTS is applied to this dataset to develop a master curve at any pivot temperature, which provides storage modulus at a much wider frequency range. The transform to time domain is an improper integral over the range $(0, \infty)$ so the experimental data is fitted to a mixture of sigmoidal functions. This choice of fitting function is motivated by the thermodynamic restrictions on the complex modulus. The transform is then evaluated numerically to obtain the relaxation function. A convolution-like integral is then used to obtain the stress history from a given strain history. This technique is used to develop simulated stress-strain curves at different strain rates, which are used to calculate the secant modulus of elasticity as a function of the applied strain rate. The trends predicted based on DMA results aligns closely with experimental results obtained from tensile testing. The method is applied to vinyl ester (VE), polycarbonate (PC) and high density polyethylene (HDPE)/fly ash composites to cover a wide range of engineering polymers and composites to validate the method.

2 MATERIALS AND METHODS

2.1 Materials

Neat Polycarbonate (PC) sheets ($18 \times 12 \times 0.125$ in³) were purchased 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 plate was fabricated by casting in aluminum molds and curing at room temperature for 24 hours and at 90 °C for 1 hour. An Othermill Pro CNC (Other Machine Co, Berkeley, CA, USA) was used to cut samples of vinyl ester and polycarbonate for DMA testing, with dimensions $35 \times 11.64 \times 2.84$ mm³. For the composites, HDPE of grade HD50MA180 supplied by Reliance Polymers, Mumbai, India was used as the matrix material. The HDPE had a melt flow index of 20 g/10 min (190°C/2.16 kg) and a mean molecular weight of 97,500 g mol⁻¹.

Cenospheres of CIL-150 grade, supplied by Cenosphere India Pvt. Ltd., Kolkata, India, are used as hollow fillers. Cenospheres are used in the as-received condition, without any surface treatment. Chemical, physical and sieve analysis results on the same type of cenospheres have been reported previously [20]. The cenospheres primarily comprise of alumina, silica, calcium oxide and iron oxides. Cenospheres were used in 20 and 40 wt.% in HDPE to fabricate two types of syntactic foams named HDPE20 and HDPE40, respectively, on a polymer injection molding (PIM) machine (Windsor, 80 ton capacity). Operating and processing parameters of the PIM machine were optimized in a set of earlier studies [21-24] and were set at 160°C temperature and 30 kg/cm² (2.9 MPa) pressure. Samples of dimensions $60 \times 12.7 \times 3.3$ mm³ were molded. The length of the specimens is later reduced by cutting

with a diamond saw to 35 mm for DMA testing. Samples for tensile testing were also injection molded, with their geometry following ASTM D638. The microstructure of the HDPE/fly ash composites is shown in Figure 1. The objective of the present study is to validate the elastic modulus recovered from the DMA data using the transform developed in this work with the elastic modulus recovered from tensile tests conducted at various strain rates. Therefore, the quality of the composite material in terms of particle size or wall thickness variation and particle crushing during processing is not relevant for this work as long as the particle distribution is homogeneous. Analysis of the density of the fabricated syntactic foams is presented in Table 1 but no further discussion on the material quality, particle crushing and void content is provided.

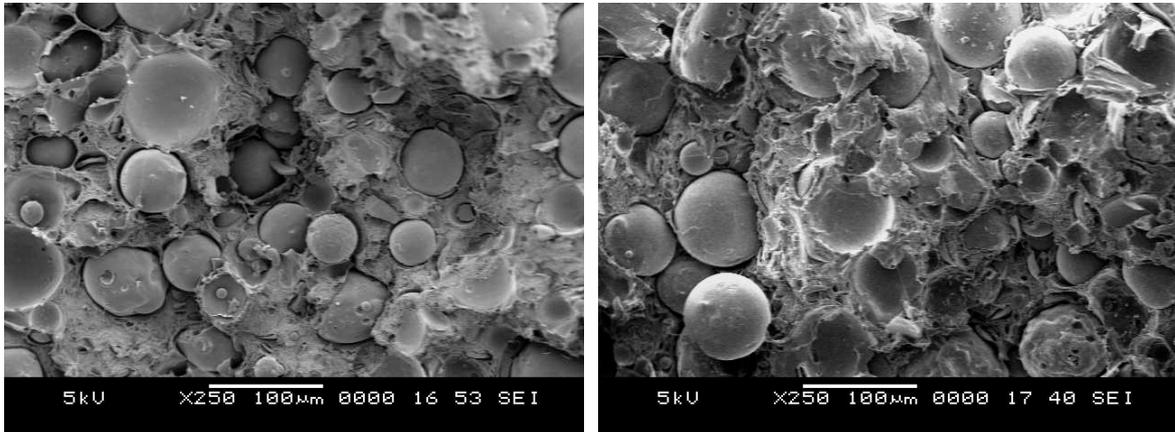


Figure 1. Microstructures of HDPE/fly ash syntactic foams containing (left) 20 wt.% and (right) 60 wt.% fly ash hollow particles.

Table 1. Density analysis of HDPE/fly ash syntactic foams for calculation of fly ash particle breakage during fabrication process.

Syntactic foam type	Φ_f	Density (g/cm ³)		Cenosphere failure during fabrication (%)
		Measured	Theoretical	
HDPE20	0.229	1.0159±0.0016	0.9976	1.83
HDPE40	0.442	1.0078±0.0036	0.9430	6.87
HDPE60	0.664	1.0219±0.0071	0.8923	14.5

* Φ_f = Cenospheres by volume %.

2.2 Dynamic mechanical analysis

Viscoelastic characteristics of the test specimens are evaluated by conducting DMA experiments using a Q800 (TA Instruments, New Castle, DE, USA) dynamic mechanical analyzer. Testing was conducted in two phases. The first phase of testing is conducted by ramping temperature at 1°C/min from -100°C to 150°C while fixing the frequency at 1 Hz, while during the second phase frequency sweeps are conducted at 5°C temperature incremental steps from -10°C to 140°C (the upper limits of the temperature ranges varied depending on the location of the melting/glass transition in each material, as testing was stopped around the onset of that transition). Thermal equilibrium at each step is attained by soaking the specimen for 8 minutes. Viscoelastic data is generated at 20 discrete frequencies within a logarithmic range from 1 to 100 Hz at each temperature step.

2.3 Tensile Testing

ASTM 638 was followed for tensile testing. Testing was conducted at four strain rates ranging from 10⁻⁶ to 10⁻³ s⁻¹. Testing was stopped at 5% strain or failure, whichever occurred first.

3 RESULTS AND DISCUSSION

Data from the temperature sweep are used to find the thermal transitions of the material. Around the transition temperatures, the frequency sensitivity is maximum, so the transition points are used to determine the temperature ranges for the frequency sweeps. Tests at temperatures far from the transitions do not lead to a richer master curve, and are resource intensive to conduct, so for practical reasons the test ranges should be restricted to encompass the transitions. For PC an α -transition was observed at around 149 °C, and a β -transition was observed at -100 °C. For VE, α and β -transitions were observed at 121 °C and -75 °C, respectively. Here, we term the glass transition to be the α -transition (note that in some literature, the ordering of naming is reversed and glass transitions are called γ -transitions). The storage modulus decreases at a gradual rate with increasing temperature but decreases rapidly after α -transition temperature.

Using the TTS principle, the E' frequency sweeps from different temperature are combined to form an E' master curve over a wide frequency span at a single temperature. Master curves for PC and VE are shown in Figure 2, and master curves for the HDPE/fly ash composites are shown in Figure 3. As these master curves cover a wide range of frequencies (over 20 decades in most cases), they can be assumed to adequately characterize a material viscoelastic function [25].

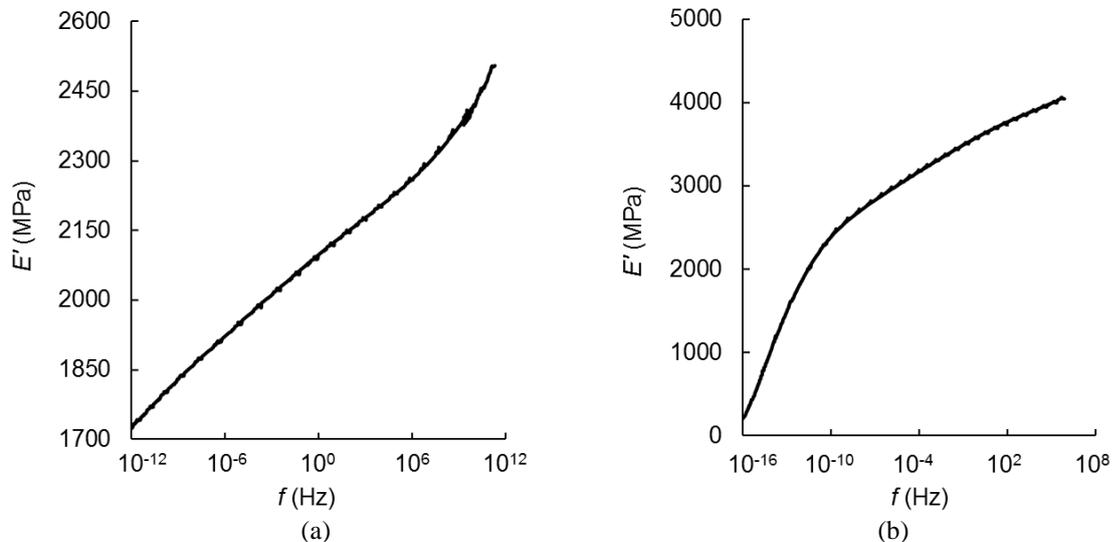


Figure 2. Storage modulus master curves at 20 °C for (a) polycarbonate and (b) vinyl ester.

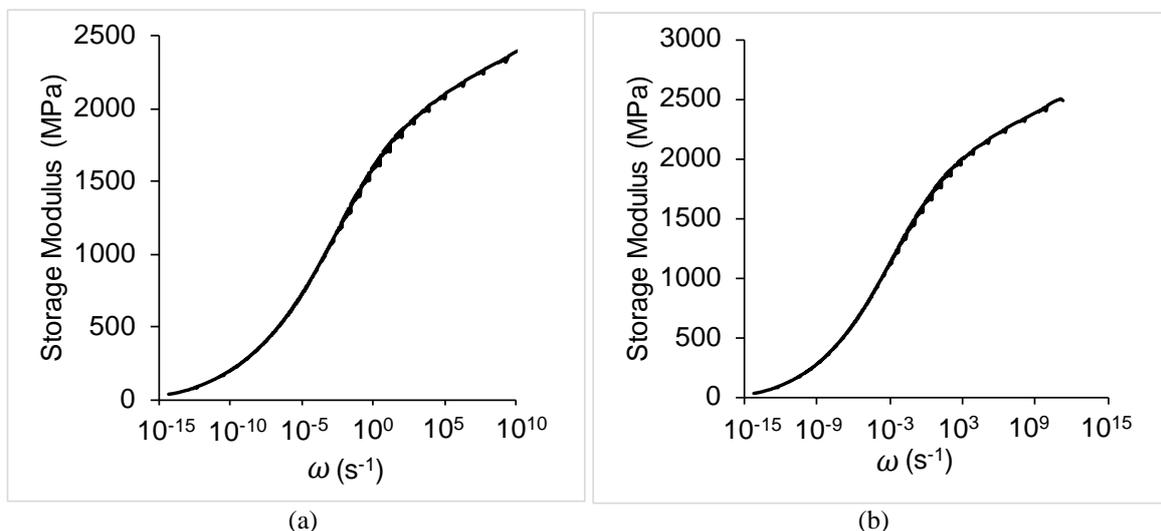


Figure 3. Master curves for HDPE/fly ash composites containing (a) 20 wt.% and (b) 40 wt.% fly ash.

The WLF formula is used to generate factors used for shifting adjacent E' functions on the frequency axis to construct a master curve for E'' for a selected temperature. Good alignment is observed (not shown, for brevity), which confirms that the material is thermorheologically simple to the extent needed for TTS to be applicable.

According to viscoelasticity theory, any one of the viscoelastic functions fully characterizes the viscoelastic response.¹ An integral transform from the theory of viscoelasticity is used to convert the frequency dependent master curve into a time-domain relaxation function $E(t)$ [26] using the integral transform given as:

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

where ω represents the angular frequency and t represents time. The master curve for E' is fitted to a mixture of sigmoidal functions of $\log(\omega)$ of the form

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

where $\log(\omega)$ represent the natural logarithm and the c 's represent the coefficients for the fit function. This allows extrapolation of the experimental data over all frequencies, as needed for the improper integral in the transform. N is determined by the number of smooth step transitions in the E' function, which also equals the number of peaks in the E'' function. Master curves for E'' for VE and PC showed two peaks, while master curves for HDPE/fly ash composites showed one peak. Therefore, for PC and VE, $N = 2$ was used; for the HDPE composites $N = 1$ was used in fitting the data. The R^2 values of the fit function for all materials are above 0.99, which indicates the function is well fitted. This fit function

is positive for all frequencies, as required by thermodynamics, only when $c_1 \geq \sum c_{j1}$, which is required to produce a physically sensible function for $E(t)$ [27]. However, this constraint is not imposed on the data in this case because it is observed that while negative storage moduli are encountered, it occurs only at such low frequencies that it does not impact the integration. Numerical experiments were conducted to test the sensitivity to the negative storage modulus at low frequency and less than 0.1% error in the short-time (order of seconds) relaxation function values was found as compared to integrating without the negative modulus values.

The fitted E' master curve for PC is non-negative at all frequencies using the determined fit coefficients, while that for VE and HDPE/fly ash violated the nonnegativity requirement below 10^{-18} Hz; this causes $E(t)$ to become negative at times on the order of millions of years and can be neglected in the calculations of $E(t)$. In addition, the calculated values of $E(t)$ for both materials satisfy the criteria of fading memory and nonnegative stored and dissipated energy [27] for all times computed, given as

$$E(t) \geq 0, \quad dE(t) \leq 0, \quad d^2E(t)/dt^2 \geq 0 \quad (3)$$

According to [26] the time-domain function is capable of deriving a stress history from a known strain history using the Stieltjes convolution integral:

$$\sigma(t) = E \times d\varepsilon = \int_{-\infty}^t E(t-\tau) \frac{d\varepsilon(\tau)}{d\tau} d\tau \quad (4)$$

where σ , ε , and τ represent stress, strain and the time variable used for integration, respectively. This stress history can be used to predict numerous elastic mechanical properties of a material; for

¹It is worth noting that some of the viscoelastic functions, notably the loss modulus master curve, lack information on the long-time modulus, and so can only be converted to others up to an unknown additive constant. This does not affect the transforms used here, but does explain why the loss modulus master curve cannot be used alone in finding the relaxation function.

simplicity this study will use the secant modulus of elasticity. The strain at which the secant is calculated is chosen to be within the quasi-linear initial response observed in the tensile tests. In an idealized tensile test with constant strain rate deformation at a strain rate $\dot{\epsilon}$, beginning at $t = 0$, the convolution integral simplifies to

$$\sigma(t) = \dot{\epsilon} \int_0^t E(\tau) d\tau \quad (5)$$

Comparison between the predicted values of modulus with those extracted from tension tests conducted at 10^{-6} to 10^{-2} s^{-1} strain rates showed close agreement, as shown in Figure 4 for VE and PC, and Figure 5 for HDPE/fly ash. As all tensile tests were conducted at room temperature, relatively small variation in the modulus of PC and VE are observed with increasing strain rate because these materials are in their glassy states at room temperature. The HDPE/fly ash showed stronger strain rate sensitivity at this temperature because the broad β -transition occurs just below room temperature. In both cases, the prediction accurately captured the modulus and the strength of its variation with the strain rate. The method shows promise for prediction of the creep behavior of materials, which would greatly accelerate a time consuming and expensive test protocol. There exist many approximate methods of evaluating the creep relaxation function from the relaxation function computed in this work. This function is then integrated through another simplified convolution to yield a creep strain history as a function of time and the applied stress. A potential limitation is that creep is typically accompanied by ageing, which is a nonlinear phenomenon that cannot be captured in the framework of linear viscoelasticity theory. Methods are available that use an internal variables approach to include the ageing effect, but so far determination of the ageing model and its coefficients has not been thoroughly studied [28, 29].

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 [18]. Outside this practical domain, predictions solely rely on extrapolation of the master curve which can be less accurate as the fitted function approaches the limits. The practical range for PC is from 10^{-16} to 10^9 s^{-1} and that for VE is from 10^{-21} to 10^3 s^{-1} . However, these domains are well beyond most ranges reported by literature on thermosets and thermoplastics. The method used in this work thus appears to be widely applicable across both very low rate deformation cases such as creep, up to high strain rate deformation as often encountered in vehicle structures.

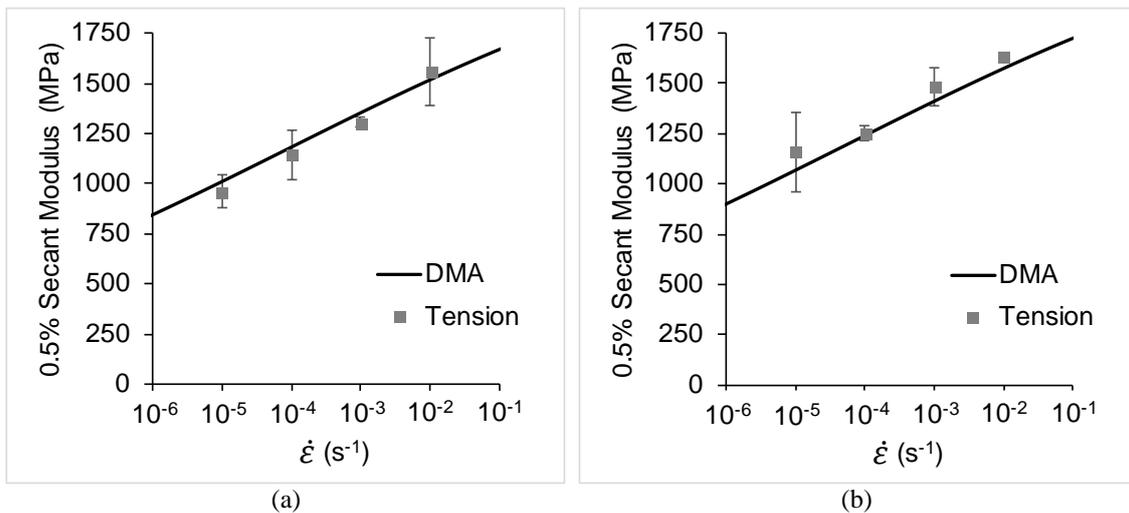


Figure 4. Modulus predictions over four orders of magnitudes of strain rates compared with tensile modulus data for HDPE composites containing (a) 20 and (b) 40 wt.% fly ash particles.

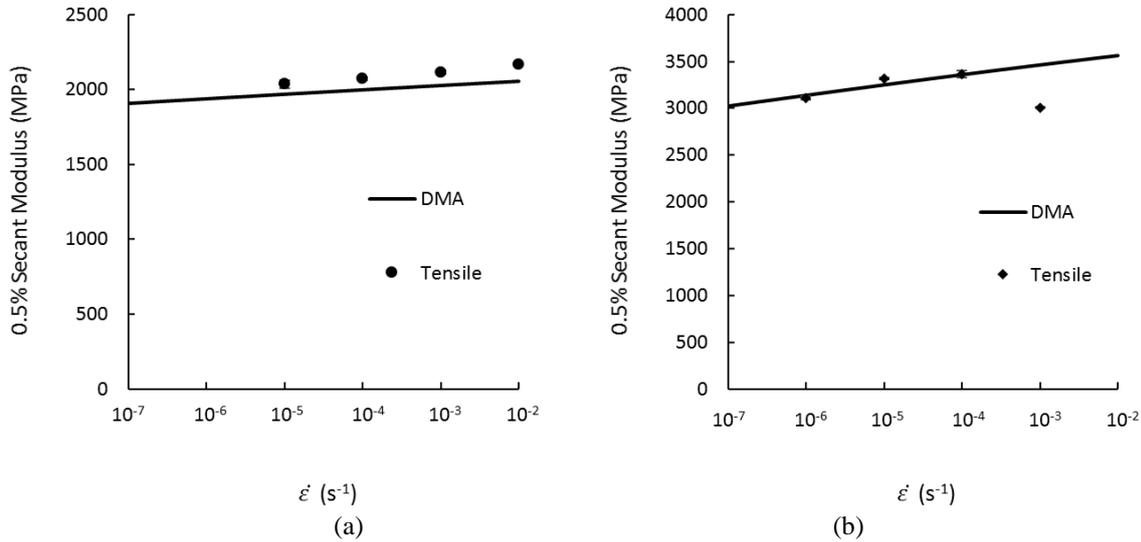


Figure 5. Comparison of secant modulus from predictions with values from separate tension test over wide range of strain rate for (a) polycarbonate and (b) vinyl ester

4 CONCLUSIONS

In this work, a method for converting the frequency- and temperature-dependent material properties measured using dynamic mechanical analysis to a time-domain relaxation function is presented. This method is able to convert the DMA data into a form that is useful for the design and engineering of structures because it yields the strain-rate material properties that can be used in making design choices. The method was validated by comparing the predictions with a separate set of extensive tensile testing. Excellent agreement was observed between the predictions of the transform method and the tensile tests. The DMA transform method has the advantage of yielding predictions of the material response over several decades of strain rate and over a wide range of temperatures from only a single specimen, tested in an experiment that takes a few hours to complete.

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