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Extracting elastic modulus at different strain rates and temperatures from dynamic mechanical analysis data: A study on nanocomposites

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ABSTRACT

Viscoelastic nature of polymers makes their properties strongly dependent on temperature and strain rate. Characterization of material properties over a wide range of strain rates and temperatures requires an expensive and time consuming experimental campaign. While viscoelastic properties of materials are widely tested using dynamic mechanical analysis (DMA) method, the frequency dependent component of the measured properties is underutilized due to a lack of correlation between frequency, temperature, and strain rate. The present work develops a method that can extract elastic modulus over a range of strain rates and temperatures from the DMA data for nanocomposites. Carbon nanofiber (CNF) reinforced high-density polyethylene (HDPE) matrix nanocomposites are taken as the study material. Four different compositions of CNF/HDPE nanocomposites are tested using DMA from 40 to 120 °C at 1–100 Hz frequency. First, time-temperature superposition (TTS) principle is used to develop an extrapolation for the results beyond the test parameter range. Then the TTS curve is transformed to a time domain relaxation function using integral relations of viscoelasticity. Finally, the strain rate sensitive elastic modulus is extracted and extrapolated to room temperature. The transform results are validated with tensile test results and the error found to be below 13.4% in the strain rate range 10^{-5} to 10^{-3} for all four nanocomposites. Since the materials are tested with the aim of finding a correlation among the test methods, the quality of the material is not a study parameter and the transform should yield accurate results for any material regardless of composition and quality.

1. Introduction

Dynamical mechanical analysis (DMA) is a well established technique for the characterization of viscoelastic properties of materials under different loading frequencies and temperatures [1]. It has numerous practical applications such as determination of thermal transition temperatures, glass transition temperature (T_g) and polymer blend miscibility in the field of polymers [2–4]. Similarly, this technique has been used extensively to characterize composites [5,6] and biomaterials [7,8] for viscoelastic properties. In this technique, the storage modulus (E') and loss modulus (E'') could be calculated from the in-phase and out-of-phase components of stress and displacement cycles [9]. The E' provides a measure of energy stored in the material while E'' refers to the amount of energy dissipated in each cycle of the sinusoidal deformation [10]. Recent studies have expanded the utility of DMA technique to other application such as estimation of spatial distribution of material properties and crack healing [11,12]. However, both E' and E'' are in frequency domain and different from elastic modulus or secant modulus in time domain, which is a major limitation of applying DMA results to mechanical design. To use the results of DMA technique for time domain applications, a method needs to be developed to transform the frequency domain results to time domain.

Several works have reported the transformation from DMA measurements into time-domain response. Jia et al. [13] developed viscoelastic constitutive relations for polyurea and its composites using experiment results. Based on the master curves of E' and E'', continuous relaxation spectra are calculated and then the time-do-

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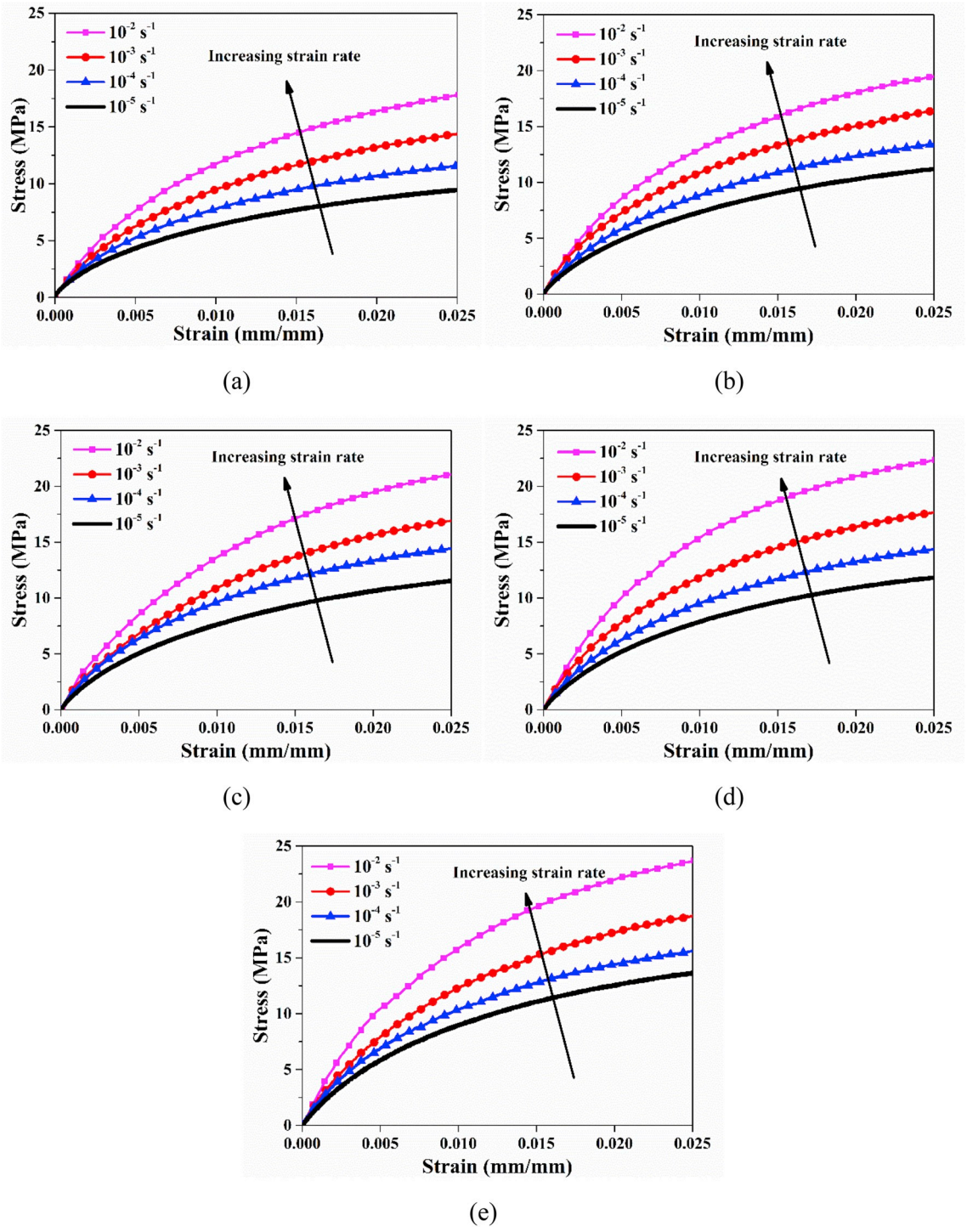


Fig. 1. A representative set of stress-strain curves for (a) neat HDPE resin and CNF/HDPE composites containing (b) 0.5 wt%, (c) 1.0 wt%, (d) 2.0 wt% and (e) 5.0 wt % CNFs.

main relaxation moduli are approximated. A transform has previously been developed to convert the frequency domain results obtained from DMA to time domain data and this method has been applied to neat polymers such as high density polyethylene (HDPE) [14], polycarbonate and vinyl ester resins [15]. The results showed that the predicted modulus closely matched with the tensile test results. Later, the same transform was also verified on hollow particle filled micro-composites called syntactic foams [16]. Compared to the tensile or compression testing for determining the elastic modulus over a range of strain rates and temperatures requiring testing a large

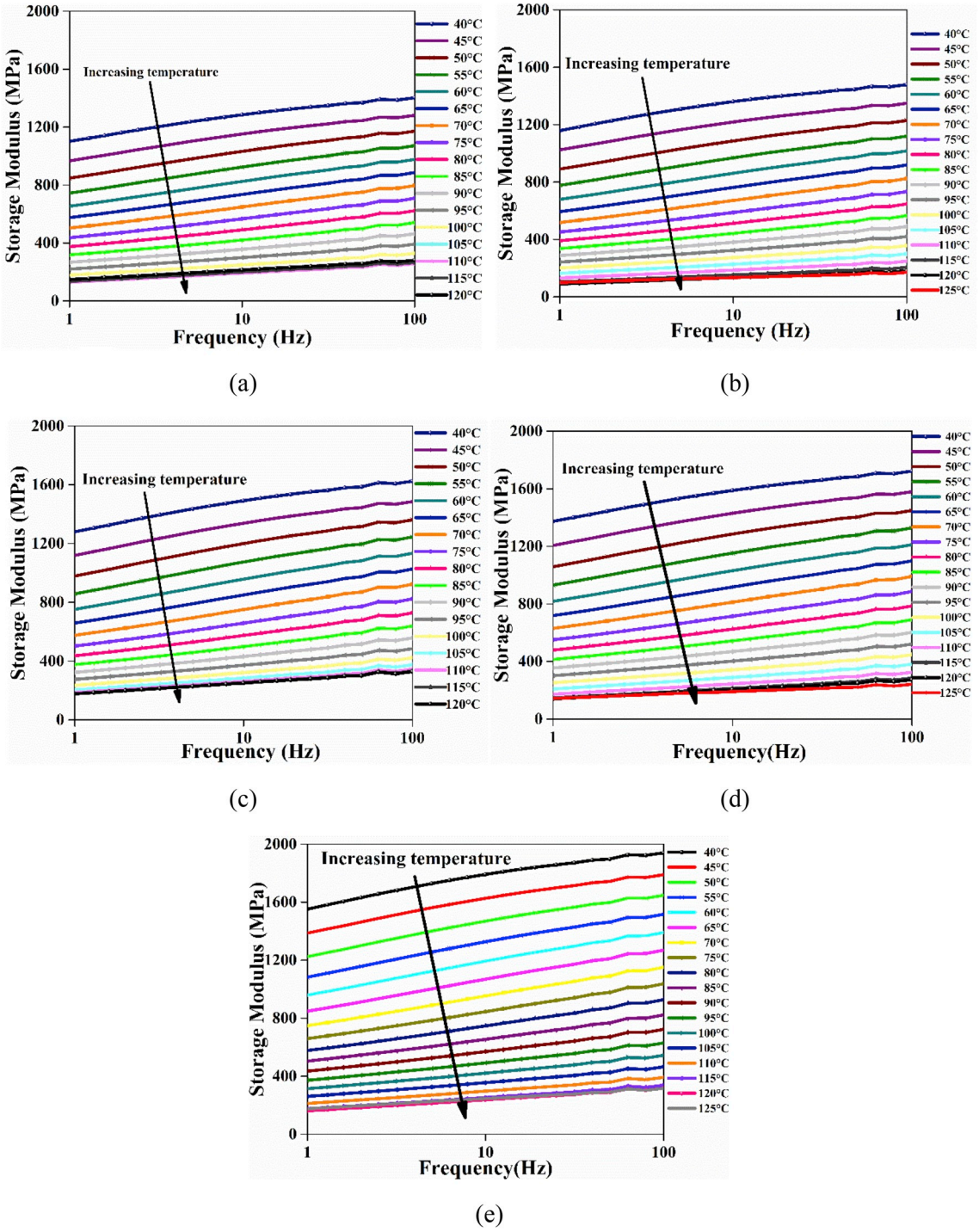
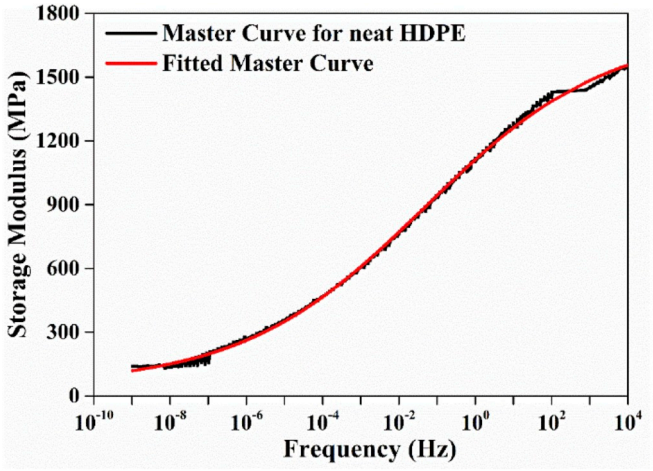


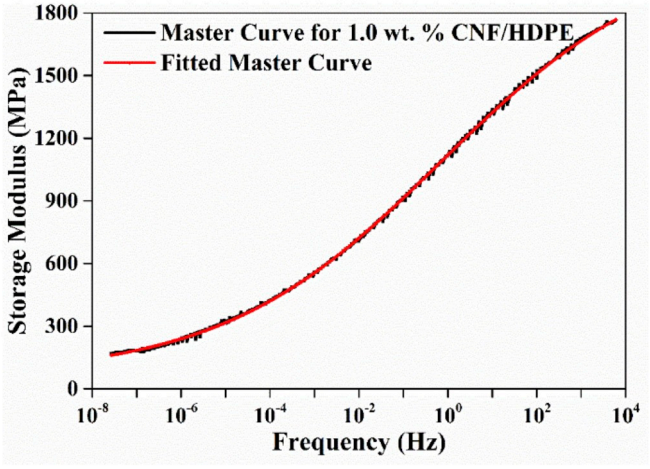
Fig. 2. A representative set of DMA frequency sweeps for (a) neat HDPE resin and CNF/HDPE composites containing (b) 0.5 wt%, (c) 1.0 wt%, (d) 2.0 wt% and (e) 5.0 wt% CNFs.

number of specimens [17–20], this method provides the same range of properties from only one specimen tested by DMA. Although this method has been used on neat polymers, it has not been applied to or validated on nanocomposites, which is the focus of the present work.

Carbon nanofibers (CNF) are attractive reinforcements for polymer matrices for improving mechanical and thermal properties [21–23]. They are useful in developing high performance composites due to their low cost and availability in large quantities [24,25]. CNF/HDPE nanocomposites are studied in this work. The tensile tests under different strain rates are conducted at room temperature and the measured



(a)



(b)

Fig. 3. A representative fitting result at 40 °C of (a) neat HDPE, (b) 1.0 wt % CNF/HDPE.

elastic modulus values are used to validate the results obtained from DMA transform. Both DMA and tensile tests are focused on measuring modulus and the results will be affected in a similar manner by factors such as CNF dispersion inhomogeneity, CNF-HDPE interfacial strength and CNF aspect ratio. Therefore, these parameters are not factors in the present study.

2. Experimental

2.1. Preparation of material

The HDPE resin is produced by Reliance Polymers, Mumbai, India. The resin is in granular form and has a mean molecular weight of 97500 g·mol^{-1}. Specimens are molded using polymer injection molding method. The injection molding parameters are optimized based on previously published optimization studies [26,27], where the temperature is set at 160 °C and the pressure is set at 2.9 MPa. Four different compositions of CNF reinforced HDPE are prepared with 0.5, 1, 2 and 5 wt % CNFs randomly dispersed in the composite. Neat HDPE specimens are also prepared using the same conditions for the comparison.

2.2. Dynamic mechanical analysis

TA Instruments (New Castle, DE) Q800 DMA is used for evaluation of the storage modulus on specimens of dimensions 60.0 × 12.7 × 2.5 mm^3. The testing is conducted in the strain control mode with a maximum displacement of 25 μm. Dual cantilever configuration with a span length of 35 mm is used for the tests in the temperature range 40–120 °C with a step of 5 °C. At each temperature step, the specimens are soaked for 5 min to ensure thermal equilibrium and then an isothermal frequency sweep is conducted at 20 discrete frequencies logarithmically spaced between 1 and 100 Hz. The test is finished when the force magnitude drops below 0.0001 N. Three specimens of each material are tested.

2.3. Tensile tests

An Instron 4467 universal test system is used to conduct tensile tests under different initial strain rates in the range 10^{-5} s^{-1} to 10^{-2} s^{-1}. The geometry of the specimens conforms to ASTM D638 standard. An Instron 25 mm gage length extensometer is attached to the test specimen to collect the strain data. For every material, four specimens are tested for each strain rate.

3. Results and discussion

3.1. Tensile test results

The tensile tests are conducted at room temperature at strain rates 10^{-5}, 10^{-4}, 10^{-3} and 10^{-2} s^{-1}, which are all within the quasi-static range. A representative set of stress-strain curves for HDPE and four types of CNF/HDPE composites is presented in Fig. 1. Since this work is only focused on the modulus, the tests results are terminated at 2.5% strain for all material types. The effect of strain rate is clearly visible due to the viscoelastic nature of the materials. Even within the slow strain rates range used for testing in the present case, HDPE resin and the nanocomposites show remarkable strain rate sensitivity. It is observed that the strength and stiffness increase with strain rate for HDPE and for all compositions of nanocomposites. At 1.0% strain, the stress at strain rate 10^{-2} s^{-1} is over 80% higher than that at a strain rate of 10^{-5} s^{-1} for the HDPE resin. The trends also show that the strength is higher for composites containing a higher amount of CNFs at the same strain level. The observed mechanical properties are a function of numerous parameters such as CNF length, dispersion efficiency, and CNF-HDPE interfacial bonding properties [28]. The strain rate is also shown to have significant effect on the measured mechanical properties and failure mechanism [29,30]. In the present material system, CNFs are randomly dispersed. Additional parameters such as alignment of CNFs can also significantly affect the properties of nanocomposites. However, these parameters are not discussed in the present case because the focus of this work is to compare the results obtained from two different characterization methods. All these materials related factors are expected to affect the results on mechanical properties obtained from both characterization methods in a similar manner and the data should be comparable. The experimentally obtained stress-strain curves do not show distinct elastic and plastic regions. Hence, secant modulus at 0.25% strain is calculated for these materials and used to validate the

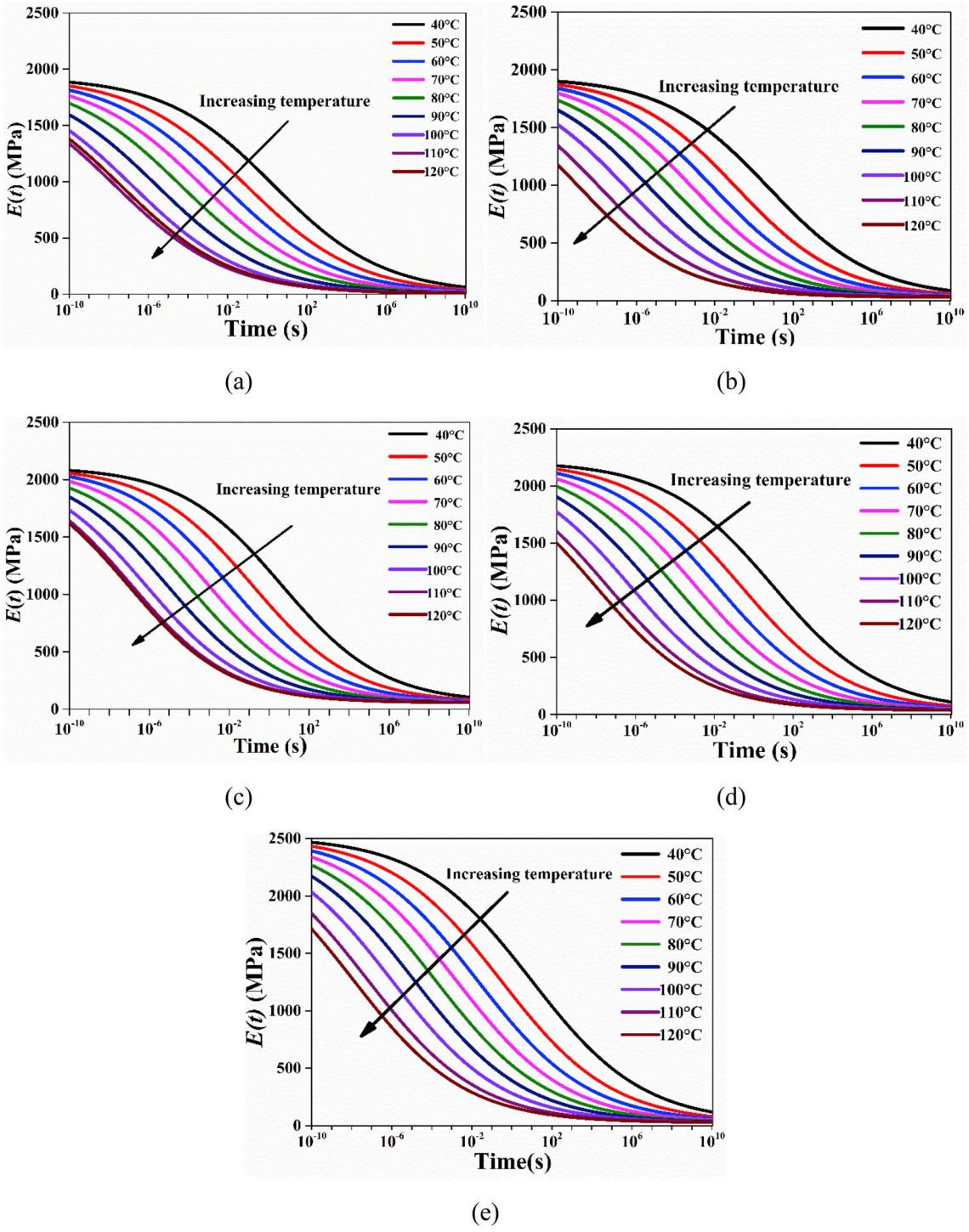


Fig. 4. Relaxation function for (a) neat HDPE resin and CNF/HDPE composites containing (b) 0.5 wt%, (c) 1.0 wt%, (d) 2.0 wt% and (e) 5.0 wt% CNFs.

modulus predictions obtained from transformation of DMA data in the following sections.

3.2. DMA temperature sweep and time-temperature superposition

The frequency domain material response is obtained from DMA by isothermal frequency sweep at various temperatures. A representative set of curves for storage moduli for neat HDPE and all types of CNF/HDPE nanocomposite are presented in Fig. 2. The results show that E' increases with frequency but decrease with temperature. The E' at 100 Hz is at least 20% higher than that at 1 Hz for each temperature for nanocomposite containing 1 wt% CNFs, which indicates the strain rate

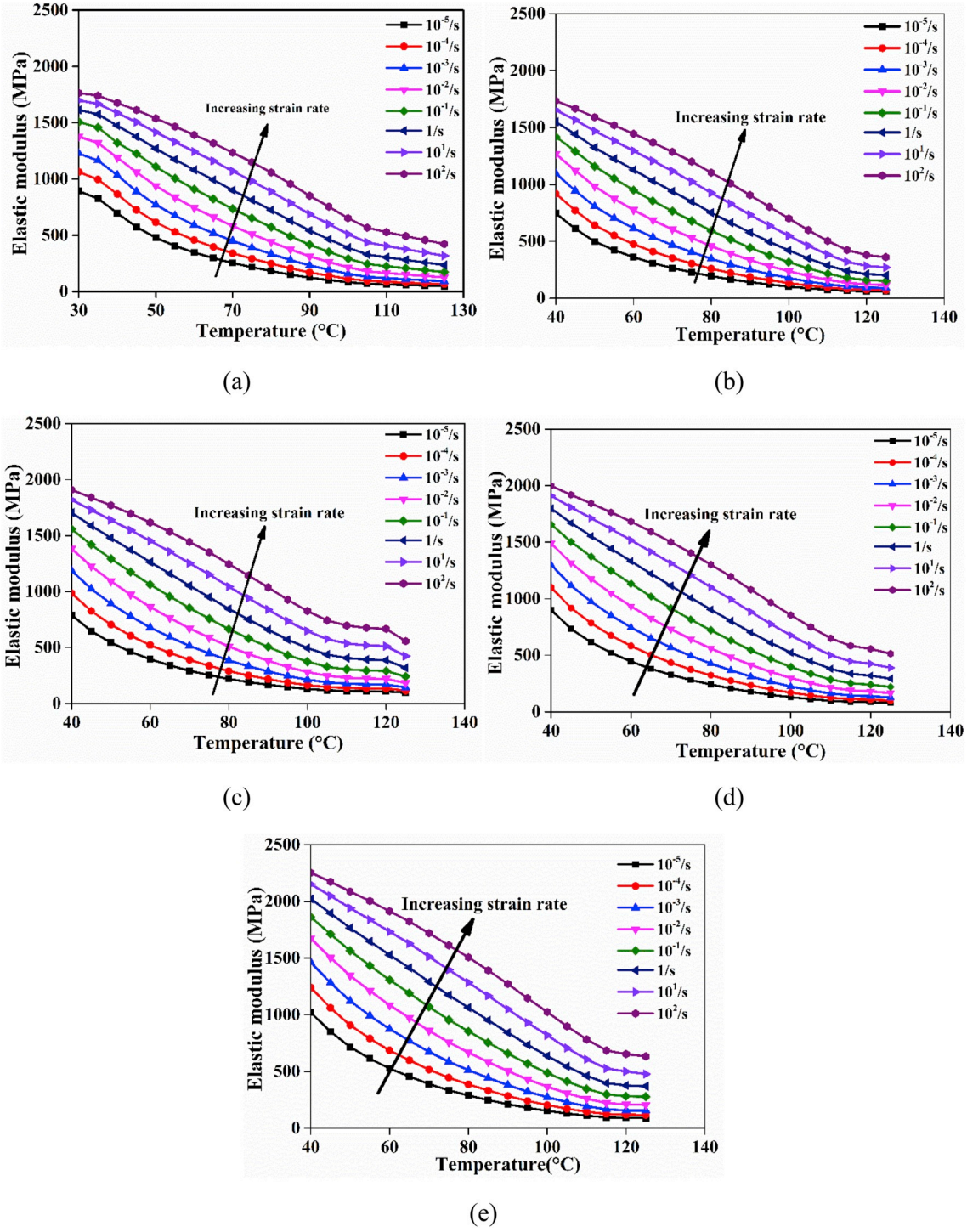


Fig. 5. Elastic modulus predicted by DMA for (a) neat HDPE resin and CNF/HDPE composites containing (b) 0.5 wt%, (c) 1.0 wt%, (d) 2.0 wt% and (e) 5.0 wt% CNFs.

sensitivity of the materials. It is also observed in this figure that the storage modulus increases with CNF content and nanocomposites have higher E' compared to the neat HDPE resin.

The results of frequency sweep are combined using Time-Temperature Superposition (TTS) principle, which allows describing the behavior of the material over a wider range of frequencies than those used in the experimental testing [31]. Using only E', the time domain relaxation modulus $E(t)$ can be determined using by Ref. [32].

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

where ω is the angular frequency and t is time. Since it is an integration from 0 to infinity, the experimental data is fitted using sigmoidal function of $\log(\omega)$ and extrapolated to zero and infinite frequencies [32]. The master curve at each temperature is fitted using the sigmoidal function

$$E' = A \tanh(B \log(\omega) + C) + D \tag{2}$$

where A, B, C, and D are the fitting coefficients and. The representative fitting result of neat HDPE and 1.0 wt % CNF/HDPE nanocomposites are shown in Fig. 3(a) and Fig. 3(b), respectively, at 40 °C. The average fitting error is found to be less than 5.2% for all materials. Other compositions present a very similar profile and are not added in this figure for brevity. The fitting function imposes that there is a smooth step transition in the E' and the function stays bounded as frequency goes to zero or to positive infinity [14,16].

The transformation in equation (1) is integrated numerically to obtain the relaxation function $E(t)$. The relaxation functions for neat HDPE and CNF/HDPE nanocomposites are presented in Fig. 4. The relaxation function has a monotonically decreasing profile with temperature and stays nonnegative as the time goes to infinity. The function $E(t)$ can be used to determine the stress with specified strain history [32].

$$\sigma(t) = E * \dot{\varepsilon} = \int_0^t E(t-\tau)\frac{d\varepsilon(\tau)}{d\tau}d\tau \tag{3}$$

where σ, ε and τ represent stress, strain and time variable. For constant strain rate deformation the time dependent stress history can be approximated as [32,33].

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

Using this transformation, the elastic response of the material can be determined at various temperatures and strain rates. The predictions of elastic modulus are defined as secant modulus at 0.25% strain according to standard ISO 527-1 [4]. Elastic moduli values predicted by DMA for neat HDPE and CNF/HDPE nanocomposites are presented in Fig. 5. Since the DMA experiments start at 40 °C, the curves of elastic moduli under same strain rate are fitted using a sigmoidal function and extrapolate to room temperature (25 °C), which is the temperature of tensile tests. Due to low glass transition temperature of HDPE, the properties of the resin and nanocomposites are strongly dependent on temperature and require applying this correction scheme for the 15 °C difference. The fitting function defined by

$$E = a\ tanh(bT + c) + d \tag{5}$$

where T is the temperature and a, b, c and d are the fitting coefficients. The fitting function has a smooth step transition and stays bounded as frequency goes to zero or to positive infinity [32]. The modulus at any temperature and strain rate can be obtained by extrapolating or interpolating the predicted modulus using Equation (5).

The elastic moduli values obtained from tensile tests are used to validate the results obtained from DMA transformation in Fig. 6. The lines predicted by DMA are the results only for one specimen but multiple specimens are tested and they showed consistent behavior. At strain rates of 10^{-5} to 10^{-3} s^{-1}, the maximum error is below 13.4% for each material, including the four compositions of nanocomposites. The transform is able to predict the modulus at a wide range of temperature and strain rate and eliminates the need for a large amount of tensile test specimens by the results obtained from a single DMA experiment.

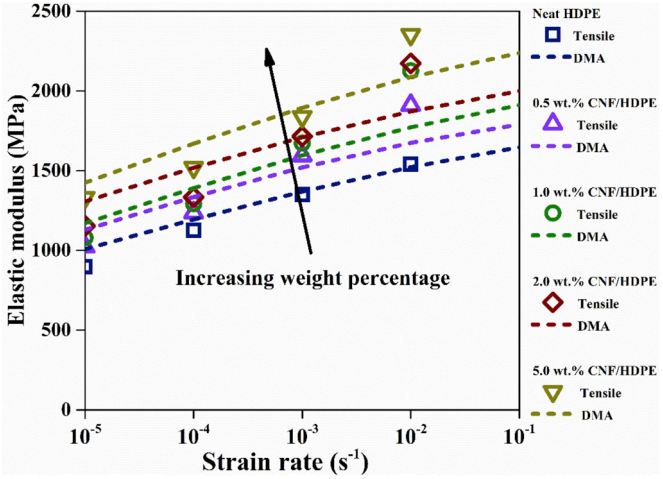


Fig. 6. Comparison of elastic modulus for CNF/HDPE composite material with different weight percentage at room temperature (25 °C).

The results included in Fig. 5 are further represented in Fig. 7 as three-dimensional contour plots, where elastic modulus is plotted with respect to strain rate and temperature. It should be noted that the entire dataset is obtained from single DMA experiment, providing much greater insight into the material system than the numerous tensile tests conducted in the validation studies. The response surface presented by these figures can be used to obtain the elastic modulus for strain rate and temperature conditions for which the material is not tested by interpolation or extrapolation. It should be noted that the results presented in Fig. 7 are limited to only within the range of temperatures where no other thermal transition exists. However, the procedure can be extended to situations where multiple transition peaks appear in the material response within the test temperature range.

4. Conclusions

In this work, a transform is developed to convert the E' obtained from dynamic mechanical analysis to elastic modulus at various strain rates and temperatures. E' is not a parameter that is used in design calculations and its use is limited in mechanical engineering and materials science. Time-temperature superposition is conducted on E' and the master curve is transformed into time domain relaxation function. Using the relaxation function, the linear viscoelastic response to a given time history and viscoelastic properties can be extracted. At strain rates of 10^{-5} to 10^{-3} s^{-1}, the maximum error is below 13.4% for HDPE resin and CNF/HDPE nanocomposites. The close agreements indicate that the transform can yield accurate predictions of the linear viscoelastic response of the materials beyond the testing temperature ranges. The availability of this transform allows converting the data obtained from one DMA experiment to a large dataset of elastic modulus over a wide range of temperatures and strain rates and eliminates the need for conducting tensile tests for the same purpose, significantly reducing the time required for materials characterization.

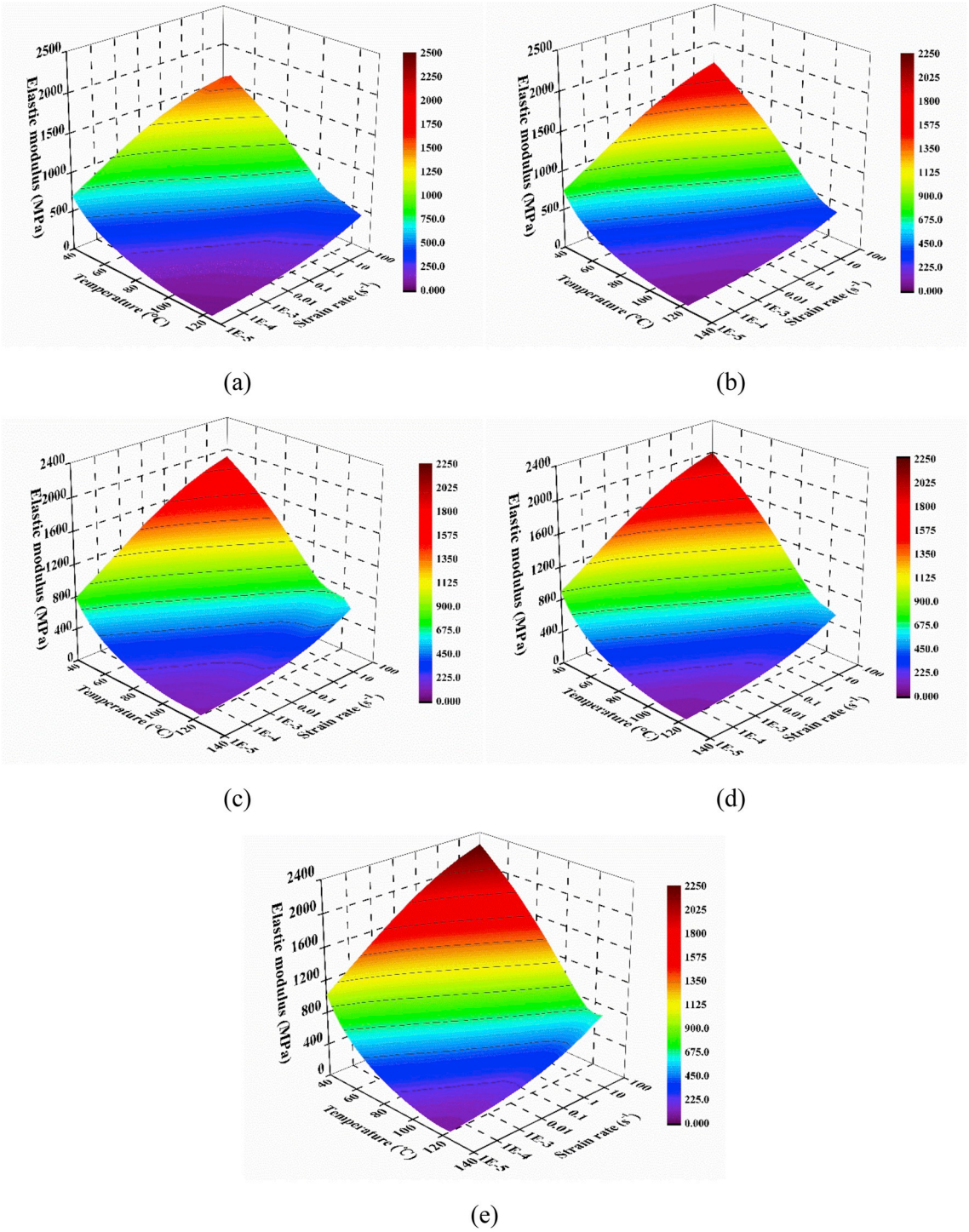


Fig. 7. Response surface of elastic modulus predicted by DMA data for (a) neat HDPE resin and CNF/HDPE composites containing (b) 0.5 wt%, (c) 1.0 wt%, (d) 2.0 wt % and (e) 5.0 wt% CNFs.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesb.2018.10.015.

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