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Determining the Shear Relaxation Modulus and Constitutive Models for Polyurea and Polyurea-based Composite Materials from Dynamic Mechanical Testing Data

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ABSTRACT

Polyurea and polyurea-based composite materials are widely used due to their excellent mechanical properties. In order to facilitate large-scale computational studies for this group of materials, a robust and standard method is needed to extract their viscoelastic constitutive parameters. In this study, frequency-domain master curves which cover a wide range of frequencies are developed using the data of dynamic mechanical analysis through time-temperature superposition (TTS). The quality of the master curves is assessed both by Kramers-Kronig relations and by comparing with the ultrasonic wave testing data. Then the time-domain relaxation modulus is obtained by the high-resolution Prony series approximated from the relaxation spectrum. To reduce computational cost, 4 to 8-term Prony series are then fitted from the time-domain relaxation modulus for a limited frequency range of interest. Both the high and low-resolution Prony series are converted back to frequency domain to compare with the master curves developed by TTS and show good agreements. This method is not limited to polyurea and polyurea-based composites and it can be applied to other similar polymer systems as well.

Keywords: polyurea, master curves, Prony series, dynamic mechanical analysis, time-temperature superposition

1. INTRODUCTION

Polyurea is an elastomeric copolymer synthesized using diisocyanates (e.g. Isonate 143L^[1], Dow Chemical) and diamines (e.g. Versalink P-1000^[2], Air Products). It has a wide range of transition zone between its glassy state and rubbery state, and its storage and loss moduli increase drastically when the frequency or pressure increases. It is an excellent material for protection from blast/impact loadings.

This work focuses on the strain rate effect on the polyurea properties in a wide frequency range. The transition zone of polyurea in the frequency domain spans more than ten decades in the logarithmic scale, and it is extremely challenging to directly measure its mechanical properties directly in such a wide frequency range. Thus alternative methods are necessary to approximate its properties. Time-temperature superposition (TTS) is applied on dynamic mechanical analysis data to get master curves. Care is taken while applying TTS and the quality of the master curves is assessed by Kramers-Kronig relations and by comparing with ultrasonic data. Based on the master curves, time-domain relaxation modulus can be calculated and optimized Prony series with desired number of terms and for the frequency range of interest can be calculated.

This study provides a consistent and convenient method to approximate mechanical properties of polyurea and polyurea composites in a wide frequency range and calculate the Prony series for specific computational applications. The same method can also be applied for some polyurea composites and other similar polymers.

2. MATERIAL FABRICATION

Pure polyurea is fabricated by mixing degassed Versalink P-1000 and Isonate 143L together under vacuum. The mixture is transferred into Teflon molds to cure in an environmental chamber for at least 2 weeks before testing. The relative humidity in the environmental chamber is kept at 10%.

The two composites are polyurea with phenolic microbubbles (PUPMB) and polyurea with milled glass (PUMG). Polyurea with phenolic microbubbles is a synthetic polyurea foam and polyurea with milled glass has both high storage and high loss moduli. The two composites are fabricated by mixing the filler material with Versalink P-1000 before degassing and then mixed under vacuum with the other component Isonate 143L. The composites are cured in the environmental chamber for at least 2 weeks before testing.

Fig. 1 shows the sample pictures of polyurea and the two polyurea composites. SEM pictures of the two composites are also showed following the sample picture.

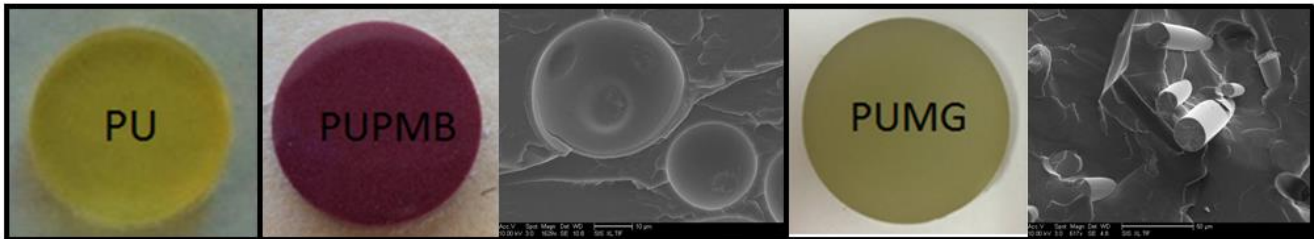


Fig. 1 Polyurea (PU), polyurea with phenolic microbubbles (PUPMB) and polyurea with milled glass (PUMG)

2. DYNAMIC MECHANICAL ANALYSIS AND MASTER CURVES DEVELOPMENT

Dynamic mechanical analysis (DMA) single-cantilever test is conducted on TA 2980 dynamic mechanical analyzer (as shown in Fig. 2), in the temperature range of -80°C – 50°C , with 3°C increment between temperature points. The test frequencies are 1, 2, 5, 10, 20 Hz. The nominal sample size is $3\text{mm}\times 10\text{mm}\times 30\text{mm}$. Storage and loss Young's moduli are measured at various temperatures and frequencies are collected by the corresponding software of the TA instrument.

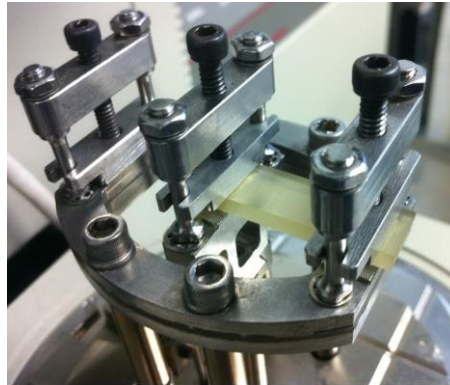


Fig. 2 Dynamic mechanical analysis single cantilever bending test

The complex Young's modulus is composed of the storage modulus and loss modulus in the following relation:

$$E^* = E' + iE'' \quad (1)$$

Time-temperature superposition is applied on the DMA data to develop master curves at the reference temperature and in a wide frequency range. The classic TTS is shown as follows:

$$E_r^* = b(T, T_0)E^*(\omega, T) \quad (2)$$

$$\omega_r = a(T, T_0)\omega \quad (3)$$

where T_0 is the reference temperature; E^* and ω are the experimental measurements; E_r^* and ω_r are the reduced modulus and frequencies of the master curve; $a(T, T_0)$ and $b(T, T_0)$ are the horizontal and vertical shift factors. The vertical shift factor is calculated as $\frac{T_0\rho_0}{T\rho}$ [3], where the density of polyurea within the DMA temperature range can be assumed to be constant. The horizontal shift factor $\log(a)$ is the average measurement from both the storage and loss moduli in order for the experimental data measured at various temperatures to connect into smooth master curves, and it can be well represented by the WLF equation [4]:

$$\log[a(T, T_0)] = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \quad (4)$$

where C_1 and C_2 are two constants.

3. MASTER CURVES QUALITY ASSESSMENTS

If the master curves of storage and loss moduli developed by time-temperature superposition are reliable, they should follow the requirements of causality in any physical system, i.e. the Kramers-Kronig relations [5, 6]. Kramers-Kronig relations show the storage and loss moduli master curves should be interrelated and be able to calculate from each other.

The storage and loss moduli master curves of polyurea and polyurea composites developed by TTS reproduce each other very well except at the two ends where error is introduced during the data extension for calculating the Kramers-Kronig relations.

Another way of assessing the master curve quality is by comparing with the ultrasonic wave measurement. The storage and loss moduli can also be acquired by ultrasonic wave measurements using the following equations [7]:

$$M' = \frac{\rho c^2(1 - r^2)}{(1 + r^2)^2} \quad (5)$$

$$M'' = \frac{2\rho c^2 r}{(1 + r^2)^2} \quad (6)$$

where c is the measured wave speed, r is the attenuation and M represents longitudinal or shear modulus based on what kind of ultrasonic wave is used for the measurement. The ultrasonic wave test is conducted between -50°C ~ 30°C at 1MHz. Young's modulus is calculated by the measured shear and longitudinal moduli. The ultrasonic Young's modulus can be shifted using the same shifting factors in TTS and compared with the DMA master curves. The storage moduli of DMA master curve and ultrasonic master curve match well with each other.

4. RELAXATION MODULUS AND PRONY SERIES

The master curves of polyurea and polyurea composites are first developed in the frequency domain. However, developing Prony series from the frequency domain is more difficult than in the time domain. Thus, master curves are first brought back to the time domain into the relaxation modulus and then Prony series for the frequency range of interest can be fitted from the relaxation modulus.

The relaxation spectrum can be calculated from the frequency domain master curves using the second approximation method by William and Ferry [8]. The relation between the relaxation spectrum Φ and relaxation modulus is:

$$E(t) = E_e + \int_0^\infty \Phi e^{-t/\tau} d\ln\tau \quad (7)$$

By using Eq. 7, the time-domain relaxation modulus which contains the information of the frequency-domain master curves can be calculated. This relaxation modulus can be used to develop 4-8 terms Prony series that insures both accuracy and computational efficiency. The form of Prony series is [3]:

$$E(t) = E_e + \sum_{i=1}^n E_i e^{-t/\tau_i} \quad (8)$$

5. DISCUSSION

This study develops a standard method to obtain master curves and Prony series of polyurea and polyurea-based composites using the experimental data of DMA test. A computational code has been developed and the flow chart of this code is shown in Fig. 3. The four inputs are the experimental DMA data, the reference temperature, the frequency range of interest and the number of Prony terms needed for the computation platform. This code automatically develops master curves, assesses their quality and generates optimized Prony series for the frequency range of interest.

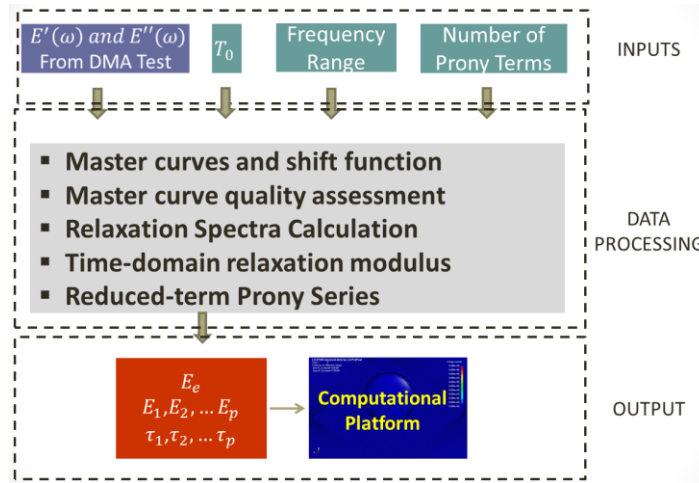


Fig. 3 Flow chart of the data processing code for developing Prony series of polyurea and polyurea-based composites

With this code, the majority of the time and efforts go into the sample fabrication and DMA testing, which is a comparatively convenient experiments in terms of characterizing the viscoelastic properties of polymers. The same method also applies for some polyurea composites and other similar polymers. Here the two composite examples are PUPMB and PUMG, one with hollow micro inclusions and one with rigid micro inclusions.

Care needs to be taken for applying TTS on heterogeneous materials. Polyurea has domain separation, and the composites materials have filler materials of different properties. However, when the relaxation mechanism of the major soft domain of polyurea and that of other domains/inclusions differ drastically, for example, when the inclusions can be regard as elastic or rigid, we still regard TTS as a useful method to get meaningful information when direct measurements are not available.

7. ACKNOWLEDGEMENT

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