Stress Responses of Polycarbosilane Melt under an Oscillating Shear Straining

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Abstract. A typical oligomers material, polycarbosilane (PCS) melt, was tested by using the advanced rheumatic expansion system (ARES) with a supplemental data acquisition card and an analog-to-digital converter (ADC). The stress response of the sample at 295 ºC to the oscillating shear straining deformation with a 50% shear and an angular frequency of 3.142 rad/s were collected, processed by using the fast Fourier transformation (FFT) technique, and compared to the conventional dynamic stress response of the melt provided by ARES. It was found that the stress response of the melt was no longer sinusoidal and that the main frequency and the amplitude of the stress response were consistent with those provided by the conventional testing method. The PCS at 295 ºC behaved like a typical yield fluid when it under the oscillating shear straining deformation with a 50% shear and an angular frequency of 3.142 rad/s.

1. Introduction
Response of a material under an applied deformation is important for practical application of the material. The rotational rheometer is usually used to measure the stress response of the polymer under shear deformation. The advanced rheometric expansion system (ARES) provides an ideal tool for the hard loading technique since ARES has two separate transducers, of which one supplies shear strain deformation and the other measures stress response of the sample. The ARES is capable of performing dynamic, steady and transient mechanical tests. The dynamic time sweep test takes successive measurements at constant temperature, frequency, and strain at a selected interval, so as to measure the periodic responses of material [1]. The stress response of the sample melt to the oscillating shear straining deformation can be obtained by dynamic time sweep test. The corresponding stress response of the melt is sinusoidal as the input sinusoidal strain provided by the conventional testing method. The maximum value of the first harmonic in computation interval is output only after the signal processed by ARES. This maximum value of the sinusoidal is named amplitude.

The rheological measurements for polymer materials melts have been well adopted. Polycarbosilane (PCS) is a typical oligomer having number average molecular weight of 1000~2000 g/mol. Its physical and chemical properties are quite different from ordinary polymers because of complex structure. It was pointed out that PCS melt was pseudo-plastic fluid with no molecular chain entanglement behavior by steady-state mode of ARES [2]. The stress response to the oscillating shear straining deformation of PCS melt, obtained by dynamic-state mode of ARES, is generally based upon the average response over measurement time. The real stress response to the oscillating shear straining
deformation cannot be presented by the conventional dynamic testing method which fits the response of linear viscoelastic model. The measurement repeatability by dynamic-state mode of ARES was improved using the shear stress-time and normal force-time curves of PCS melt [3].

In this work, the home-made PCS melt was tested by using ARES with a supplemental data acquisition card (NI USB-6001) and an analog-to-digital converter (ADC). The stress responses of the sample at 295°C to the oscillating shear straining deformation with a 50% shear and an angular frequency of 3.142 rad/s were collected. The data were further processed by using the fast Fourier transformation (FFT) technique, and compared to the conventional dynamic stress response of the melt provided by ARES. The lissajous figure has also been obtained by superimposing torque and shear strain.

2. Experimental

2.1. Material
The PCS raw samples with the softening point temperature of 215 °C were prepared according to the Yajima process. The samples were further ground by a mortar into fine powders, and then pressed into the button shaped specimens having 25 mm in diameter.

2.2. Rheological measurements
The rheological measurements were carried out by the mode of dynamic time sweep test using an advanced rheometric expansion (ARES-4400) manufactured by TA Instruments. The dynamic time sweep test was conducted at constant temperature, frequency, and strain. The oscillating shear straining deformation was fixed at 50% with an angular frequency of 3.142 rad/s. The successive shear measurements were done for 1200 s at 295 °C. The parallel plate geometry with the diameter of 25 mm was used with the gap of 1 mm.

The analog-to-digital converter (ADC) is a data acquisition card that converts the analog signal of the rheometer into a digital signal. Applied shear strain signal and output torque signal were collected by the data acquisition card (NI USB-6001) which had been inserted into the back plate of ARES. The sampling rates for shear strain and torque were both 10 KS/s.

2.3. Processing methods of data and noise
All the signals obtained by the data acquisition card were represented by the voltages in order to simplify data. The voltage range of collected shear strain signals was ±5 V, corresponding to the maximum applied strain of 6.25 by ARES. The shear strain was divided by the voltage for 1.25/V. Similarly, the torque was divided by the voltage for 40 g·cm/V. The signals acquired were usually mixed with other responses, called noises. Oversampling technique was used to reduce the random noise in this work. The technique was conducted by increasing the number of sampling points and the collection density. The noises were dispersed into other frequencies by using FFT technique, while the shear strain or torque with stable frequency will be retained at the corresponding frequency.

3. Results and Discussion
The torque response to the shear time of the PCS at 295 °C was obtained under the oscillating shear straining deformation with a 50% shear and an angular frequency of 3.142 rad/s. The input shear strain was sinusoidal as illustrated in the formula (1), while the output torque was the amplitude of sinusoidal based on the formula (2) by ARES.

\[ \gamma = \gamma_0 \sin \omega t \]  

(1)

\[ M = M_0 \sin(\omega t + \phi) \]  

(2)

Where \( \omega = 2\pi f \) is the angular frequency, \( f \) is the frequency, \( \gamma_0 \) is the magnitude of the applied shear strain, \( M_0 \) is the magnitude of the torque, \( \phi \) is the phase angle, and \( t \) is the shear time. The data
measured by the conventional testing method, as given in Figure 1, is the average $M_0$ over the measurement time.

The original response of PCS sample at 295 ºC to the oscillating shear straining deformation with a 50% shear and an angular frequency of 3.142 rad/s were also collected by data acquisition card

![Figure 1](image1.png)

**Figure 1.** Torque–shear time curve of PCS melt by the conventional testing method. $\omega = \pi$ rad/s, $f = 0.5$ Hz, $\gamma = 0.5$.

![Figure 2](image2.png)

**Figure 2.** (a) Applied shear strain-time curves of PCS melt (b) The frequency distribution curve of the strain amplitude after FFT smoothing.
preinserted. Figure 2(a) shows part of the red curve selected from the applied shear strain signal of PCS melt. The blue curve smoothed by FFT technique with the noise removed by smoothing is also displayed in Figure 2(a), which is almost fully overlapped with the red curve. It is evident that the applied shear strain was a simple sinusoid whether smoothed or not. The FFT result of the shear strain is presented in Figure 2(b), providing the frequency distribution curve of the strain amplitude, named the frequency spectrum of the strain. It can be seen that the two obvious frequencies in the spectrum were the measuring frequency of 0.5 Hz and the bias voltage of 0 Hz. And other frequencies of relatively prominent noise or higher harmonics were not found. This result also confirmed that the applied shear strain was a pure sinusoid.

Figure 3(a) shows the corresponding torque-time response of PCS melt to the oscillating shear straining deformation with a 50% shear and an angular frequency of 3.142 rad/s by data acquisition card. It can be found that the stress response of PCS melt was no longer sinusoidal compared to the applied shear strain, while the burrs of the curve indicated that the noise had obvious effect on the output torque signal. The torque curve after FFT processing was much smoother than the original one, but it was still not a normal sinusoidal curve. While the proportion of the remained noise was relatively large. The frequency spectrum of the torque after FFT smoothing has also been presented in Figure 3(b). Other response frequencies, including the higher harmonic frequencies and the non-multiple frequencies, were also found in the spectrum in addition to the main frequency of 0.5 Hz and the bias voltage of 0 Hz. These higher harmonics were also special responses of the PCS melt. It can be seen that the frequencies of higher harmonics have reached at least 15 harmonics by peak detection, with the corresponding frequency of 7.5 Hz. The responses above 10 Hz have been removed after FFT smoothing, so as to retain the main response frequency and to remove most of the noises. The main frequency of 0.5 Hz and the amplitude of the stress response after FFT smoothing were consistent with

![Figure 3](image-url)

**Figure 3.** (a) Torque-time response curves of PCS melt (b) The frequency distribution curve of the torque amplitude after FFT smoothing.
those provided by the conventional testing method as illustrated in Figure 1. Figure 4 displays the lissajous figure that was trajectories of torque and shear strain in mutually perpendicular directions. In the figure, the red curve represents the raw data for torque and shear strain collected from 50 s to 250 s (100 cycles) by data acquisition card, while the blue curve is the results corresponding to FFT smoothing of the raw data. The green curve exhibits the main frequency (first harmonic) of FFT smoothing curves which is 0.5 Hz. Apparently, the large noises of the red curve covered a full range. While the blue curve obtained after FFT smoothing was relatively smoother and more convergent. However, there were still some divergences in the blue curve as the variation of cycles. It was mainly because the noises below 10 Hz have not been removed by FFT smoothing. The blue curve revealed the true responses of PCS melt under the oscillating shear straining deformation. The green curve was the response under ideal condition of linear viscoelastic model, corresponding to the data processing method of ARES. It can be found that the stress response of PCS melt under the oscillating shear straining deformation was not the first harmonic response of linear viscoelastic model. The PCS behaved like a typical yield fluid at 295 °C when it under the oscillating shear straining deformation with a 50% shear and an angular frequency of 3.142 rad/s from the lissajous figure.

![Figure 4. The lissajous figure of torque and shear strain (100 cycles).](image)

### 4. Summary

The stress responses of the home-made PCS sample at 295 °C to the oscillating shear straining deformation with a 50% shear and an angular frequency of 3.142 rad/s were collected by data acquisition card. The data were processed by using the fast Fourier transformation (FFT) technique, and compared to the conventional dynamic stress responses of the melt provided by ARES. The stress response of PCS was no longer sinusoidal and the main frequency and the amplitude of the stress response were consistent with those provided by ARES. The lissajous figure revealed the PCS melt behaved like a typical yield fluid when it under the oscillating shear straining deformation with a 50% shear and an angular frequency of 3.142 rad/s.

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### References

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