**Supporting Information**

**Nonlinear viscoelasticity of pre-compressed layered polymeric composite under oscillatory compression**

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**Introduction to the analyzing methods for nonlinear viscoelasticity**

If we superimpose a fixed pre-compression and a single-harmonic sinusoidal compression on the sample (Fig. 1), the displacement of the upper surface of the sample can be described as:

, (1)

where *u*0 is pre-compression, Δ*u* is oscillatory amplitude, and *f* is oscillatory frequency. The steady state response force can be written as:

, (2)

where *F*0 is the steady-state static force, which depends only on the pre-compression (here we do not account for stress relaxation, i.e., *F*0 is a time-independent constant) and Δ*F* depends on the pre-compression, oscillatory amplitude, and oscillatory frequency. If the material is linear viscoelastic, Eq. (2) translates only into a first-order term. The nonlinear part, depending on the type of nonlinearity, might modify this first-order term and also be reflected in higher-order items that can be analyzed through the two techniques that are investigated here. If we analyze the response-force signal in the frequency domain by FT, it is possible to quantitatively analyze the nonlinear characteristics of the structural composite under oscillatory compression. The asymmetry of the Lissajous curve induced by the superimposition of pre-compression causes all the higher-order harmonics (both of odd and even terms) appear.

Because FT is a linear operation, the linear superimposition characteristics will not change from the time domain to the frequency domain [28]. The zero-order frequency item in the frequency domain originates from static force and thus is not considered in an analysis of the dynamic mechanical properties. The harmonics relevant to oscillatory compression begin with the first-order term. We define the first-order term as the first (fundamental) harmonics (i.e. *S*1*(f)*). Every spectrum, *S(f)*, obtained in the frequency domain is actually a complex function with real *Re(f)* and imaginary *Im(f)* parts. We classically define the amplitude as the intensity of this spectrum:, which is also called the Fourier intensity. The change in the Fourier intensity between harmonics can be used to quantitatively characterize the degree of nonlinearity: a large ratio of high-order Fourier intensity to the first-order term indicates a large deviation from linearity (i.e. strong nonlinearity). We used the fast Fourier transform (FFT) function in Matlab R2016b to process the discrete experimental data and to calculate the relative Fourier intensities (*I*n*/I*1) by Matlab to investigate the degree of nonlinearity.



**Fig. S1** Definitions of viscoelastic stiffness (a) and dissipated energy (b) based on the Lissajous curve.

Although FT can quantitatively characterize the degree of nonlinear viscoelasticity, finding distinct physical meaning for the higher-order harmonics of a Fourier series remains difficult [28, 48]. In the Lissajous curve, two kinds of compressive stiffness (or modulus) can be defined to capture local nonlinear behavior:

 and (3)

, (4)

where *E*M is the tangent stiffness at *u*=0 and *E*L is the slope of the line connecting the origin and the point at *u*=Δ*u*, as shown in Fig. S1a. If the material is linear viscoelastic, *E*M=*E*L. Within the NVE range, we can observe strain stiffening (*E*M<*E*L ) or strain softening (*E*M>*E*L). Based on this geometrical analysis, we can define *S* (as shown in Eq. (5)) as the distortion of Lissajous curve away from a perfect ellipse, which is another parameter that quantitatively characterizes nonlinear viscoelasticity. In addition, the material characteristics (i.e. strain stiffening, linear viscoelastic, or strain softening) can be identified according to the sign of *S*.

, . (5)

Ewoldt *et al* first introduced this geometrical concept to analyze the nonlinear viscoelasticity of complex fluids under LAOS [32]. Compared with complex fluids, the dynamic mechanical behavior of viscoelastic solids under LAOC is more complicated: the superimposition of pre-compression results in asymmetry of Lissajous curve. If we divide the Lissajous curve into loading and unloading stages, the moduli can be redefined, as shown in Fig. S1a, to *S*loading and *S* unloading, respectively. These two parts of the curve can be calculated based on Eq. (5). More details, including the asymmetry of the Lissajous curve at different loading stages, about the nonlinear viscoelasticity can therefore be revealed. In addition, the dissipated energy can be calculated from the Lissajous curve as well (the formula is given in Fig. S1b). Furthermore, the asymmetry of the Lissajous curves is also an indicator of nonlinear behavior and can be represented by the proportion of dissipated energy in the loading and unloading stages.

**Quasi-static compression of layered polymeric composite**

Three different deformation regions are defined according to the compressive curves as shown in Fig. S2. At the beginning, the deformation is dominated by the soft polymeric layers, and the response force is very small. When the loading displacement increases, the constraint of the hard polymeric layer is enhanced gradually (this stage is defined as the transition region). Finally, the constraint reaches its maximum, and a coordinated deformation for all of the polymeric layers appears. The force-displacement curve in this region is approximately linear. The stiffness of the layered polymeric composite is therefore calculated as the slope of the force-displacement curve in the coordinated deformation region, as shown in Fig. S2.



**Fig. S2** The force-displacement curves of 9 layered polymeric composite under quasi-static cyclic compression. The loading condition for cyclic compression is shown in the inset.

**Influence of oscillatory amplitude on Lissajous curves at different pre-compression**

The Lissajous curves are not elliptical at large oscillatory amplitudes. A platform stage at the beginning of the Lissajous curve is found when pre-compression is 0.08 mm or 0.14mm, which is quite similar to the quasi-static loading curve presented in Fig. S2. This indicates that the deformation mechanism as shown in Fig. S2 is also applicable in dynamic mechanical tests. The platform stage disappears if the pre-compression increases to 0.20 mm, but the Lissajous curves are not elliptical. Both of the loading and unloading parts of a cycle result in concave curves, indicating that another kind of nonlinear mechanism exists under this loading condition.



**Fig. S3** The Lissajous curves of 9 layered polymeric composite at different oscillatory amplitudes. Oscillatory frequency: 0.01 Hz; Pre-compression: 0.08mm (a), 0.14 mm (b), 0.20 mm (c).

**Influence of layer number on the stiffness and dissipated energy**

Both stiffness and dissipated energy of layered polymeric composite can be adjusted by the number of layers with a fixed composition. The constraint of hard polymer to soft polymer determines the response force under the same loading conditions. A strong constraint exists in the layered polymeric composite with a large number of layers, which results in large stiffness and high dissipated energy. However, a layered polymeric composite with a strong constraint is easier to break. Thus, the stiffness and dissipated energy of the layered polymeric composite will not increase when the layer number is larger than 15. In dynamic mechanical tests, the critical layer number for structural collapse is smaller (11 layers).



**Fig. S4** The stiffness (a) and dissipated energy (b) of layered polymeric composite with different number of layers. The loading condition is the same as that shown in the inset of Fig. S1. The volume ratio of hard and soft polymers for all samples is 1:1. The dissipated energy is calculated as the average area of the last 3 loading cycles. “Odd layers-hard”: the layer number is odd and a hard polymer layer contacts the loading plate; “Odd layers-soft”: the layer number is odd and a soft polymer layer contacts the loading plate; “Even layers-hard”: the layer number is even and a hard polymer layer contacts the loading plate; “Even layers-soft”: the layer number is even and a hard polymer layer contacts the loading plate.

**The dynamic mechanical response of an 11 layered polymeric composite**

Force distortion (Fig. S5a) in the force-time curves and flat curves in the Lissajous curves (Fig. S5b) at large oscillatory amplitudes were determined for an 11 layered polymeric composite. The forces in the region of the flat curve are close to zero, which is similar to the hard polymer. However, extrusion of soft polymer and delamination of the sample was found, as shown in Fig. S6b and S6c. Therefore, the nonlinear mechanism of the 11 layered polymeric composite at large oscillatory amplitude is different from that of the hard polymer.



**Fig. S5** Time-dependent response force during one loading cycle of an 11 layered polymeric composite at different oscillatory amplitude (a); The Lissajous curves of 11 layered polymeric composite at different oscillatory amplitudes (b). Oscillatory frequency: 0.01 Hz; Pre-compression: 0.20 mm.

**The fracture modes of a layered polymeric composite**

Fracturing of layered polymeric composite is closely related to the compressive loading. Without compression, the hard and soft polymers are arranged crosswise (Fig. S6a). As the compressive loading increases, four different kinds of fracture modes appear in sequence as shown from Fig. S6b to S6f. At first, the soft polymer is extruded between the hard layers (Fig. S6b). Then, the hard layers become delaminated (Fig. S6c). With further compression, transverse cracks appear in the hard layers (Fig. S6d). If we observe the hard layer perpendicularly, some transverse cracks are filled with soft polymer, as shown in Fig. S6d. Finally, the sample is compressed into pieces, indicating that the layered polymeric composite completely fails to resist the compressive loading in this situation (Fig. S6f). We note that the structures presented in Figs S6d, S6e, and S6f were not produced with the dynamic mechanical tests in this study, they were observed at different quasi-static compressive stages. Because it is difficult to conduct the in situ compressive experiment, one-to-one correspondences between the structural images and the compressive curve cannot be made. However, the fracture process as shown in Fig. S6 is in sequence with the increased compressive loading. We can therefore deduce the nonlinear mechanism by combining the structural images, the dynamic response curves (Lissajous curves and response force-time curves), and its corresponding nonlinear viscoelastic parameters of the material (*I*2*/I*1 and *S*).



**Fig. S6** Structural images of a layered polymeric composite at different compressive stages taken by an optical microscope (Carl Zeiss Microscopy GmbH, Gottingen, Germany). The scalebar is 1 mm.