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

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Abstract

Describing nonlinear viscoelastic properties of polymeric composites when subjected to dynamic loading is essential for development of practical applications of such materials. An efficient and easy method to analyze nonlinear viscoelasticity remains elusive because the dynamic moduli (storage modulus and loss modulus) are not very convenient when the material falls into nonlinear viscoelastic range. In this study, we utilize two methods, Fourier transform and geometrical nonlinear analysis, to quantitatively characterize the nonlinear viscoelasticity of a pre-compressed layered polymeric composite under oscillatory compression. We discuss the influences of pre-compression, dynamic loading, and the inner structure of polymeric composite on the nonlinear viscoelasticity. Furthermore, we reveal the nonlinear viscoelastic mechanism by combining with other experimental results from quasi-static compressive tests and microstructural analysis. From a methodology standpoint, it is proved that both Fourier transform and geometrical nonlinear analysis are efficient tools for analyzing the nonlinear viscoelasticity of a layered polymeric composite. From a material standpoint, we consequently posit that the dynamic nonlinear viscoelasticity of polymeric composites with complicated inner structures can also be well characterized using these methods.

Keywords

Nonlinear viscoelasticity; Layered polymeric composite; Fourier transform; Geometrical

nonlinear analysis; Oscillatory compression

1. Introduction

Using a composite with layered structure is a simple but effective way to isolate creature or instrument from vibration or impact [1-5]. Indeed, layered structures are common in biological materials [6-10] and bio-inspired composites [11-18]. When used as isolator or damper, a layered structural composite can experience both static loads (pre-strain) and dynamic loads (oscillatory tension or compression) [19-25]. The composite falls into the nonlinear viscoelastic (NVE) range if a large amplitude oscillatory compression (LAOC) is applied [24, 26]; nonlinear viscoelasticity usually results from the change or damage to the inner structure of the composite [27]. Therefore, the nonlinear viscoelastic properties of layered structural composites is very important to material design or structural monitoring.

Nonlinear viscoelasticity appears when the dynamic moduli (i.e. storage modulus and loss modulus) obviously vary with the increasing oscillatory strain amplitude, which also means that the Lissajous curve (the stress-strain curve in a stable oscillatory cycle) is no longer perfectly elliptical. In such a situation, the storage moduli defined within linear viscoelastic range lose their specific physical meaning [28]. This phenomenon is known as the Payne effect [29] which is used to determine the NVE range [24, 26, 30, 31]. However, Payne effect can only indicate that the nonlinearity appears but cannot tell how much the nonlinearity is. That is to say, if we expand the different orders in the nonlinear viscoelastic response (Eq. 2 in supporting information), the storage modulus which we use in Payne effect is actually the first-order term, the higher-order terms cannot be quantitatively characterized from Payne effect. Moreover, the nonlinearity sometimes cannot be captured and predicted by the Payne effect. Ewoldt *et al* found that although the Lissajous curves of pedal mucus (a kind of complex fluid) were obviously distorted, the Payne effect was not obvious (i.e. the storage modulus was independent of the oscillatory amplitude) [32]. The

Lissajous curve might be a more efficient tool than analysis based on the classical Payne effect to reveal nonlinear viscoelasticity. However, Lissajous curves are currently mostly used in a qualitative way. Direct identification of parameters based on Lissajous curves for quantitative descriptions of nonlinear viscoelastic behaviors would be useful in exploring the nonlinear viscoelastic mechanism.

The stress response in the NVE range is no longer single-harmonic sinusoidal. Expressing this response as a Fourier series and Fourier transforms (FT) makes a discussion of the nonlinearity in the frequency domain possible [33]. Wilhelm called this approach “Fourier-transform rheology” (FTR) [34]. FTR has been widely used in recent years to analyze the nonlinear viscoelasticity of complex fluids (such as polymer solutions [35], polymer melts [36], and emulsions [37]) under large amplitude oscillatory shear (LAOS) [38-41]. Because the Lissajous curve in shear rheology is odd symmetric, only odd-harmonic items exist in its Fourier series. In the extensional [42, 43] or squeezing rheology [44-46], the situation is more complicated: all higher-order harmonics appear due to the asymmetric Lissajous curve [47]. Fortunately, the nonlinear viscoelasticity in all such situations can be well detected and quantitatively characterized by FTR.

However, FT is essentially a mathematical tool, the physical interpretation of the higher-order harmonics cannot be clarified by FT [28, 48]. Ewoldt *et al* introduced a geometrical nonlinear parameter to define the nonlinear viscoelasticity of a complex fluid under LAOS [32]. They found that tangent modulus at the minimum strain and the secant modulus at the maximum strain can capture the local nonlinear behavior of the Lissajous curve. In addition, the distortion of the Lissajous curve away from the perfect ellipse can be well described by the dimensionless index of nonlinearity. The parameters defined in this method not only have specific physical interpretations, they also reveal the intrinsic characteristics of the fluid (i.e. strain stiffening and strain softening). Geometrical analysis is

therefore another effective way to analyze the nonlinear viscoelasticity of complex fluids.

Few studies analyzing the nonlinear viscoelasticity of viscoelastic solids using FT or geometrical nonlinear analysis have been published, especially when the solids are under complicated loading conditions. The biggest difference between viscoelastic solids and complex fluids is that pre-compression of the solid is needed to avoid separation between the loading plate and the sample during the test, which means that a static stress is superimposed on the dynamic response stress and that the Lissajous curve is consequently completely asymmetric. It is worth to mention that these methods are intended to be general and can be used to analyze the dynamic nonlinear viscoelasticity of any viscoelastic solids. Applications can be as diverse as polymer/graphene composites [49], blend composites [50,51], or alternating multilayered materials [52]. Here, we use FT and geometrical nonlinear analysis to analyze the nonlinear viscoelasticity of a pre-compressed layered polymeric composite under LAOC. We also discuss the influence of loading conditions and the structural parameters of the polymeric composite on the nonlinear viscoelasticity.

2. Experimental details

Layered structural composites with two different photo-sensitive polymeric components (Fig. 1) were prepared on a 3D printer (Objet260 Connex, Stratasys Ltd). Tangoblack+ (compressive stiffness, the slope of the force-displacement curve in the coordinated deformation region, as shown in Fig. S2: 7.86×10^4 N/m) was chosen as the soft polymeric phase and the hard polymeric phase was Veroblack (compressive stiffness: 2.21×10^7 N/m). The inner structure of the layered polymeric composite was determined by the volume ratio and the number of layers. Two groups of samples were designed. The first group was prepared with the same number of layers (9 layers) but different volume ratio (hard polymer: soft polymer=5:1, 4:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:4, 1:5); the second group was prepared with the same volume ratio (hard polymer: soft polymer=1:1) but different numbers

of layers (3, 5, 7, 9, and 11). The dimension of each sample was $13 \text{ mm} \times 13 \text{ mm} \times 4 \text{ mm}$ and the thickness of each layer for the same polymer are equal.

Fig. 1 The experimental setup and loading mode.

The Instron E10000 universal testing system (dynamic load capacity: $\pm 10 \text{ kN}$; static load capacity: $\pm 7.1 \text{ kN}$) was used for the static and oscillatory compressive tests, as shown in Fig. 1. The loading mode is also illustrated in Fig.1, the pre-compression was adjusted manually via the Console software while the oscillatory compression was set by the WaveMatrix software. The loading conditions including pre-compression, oscillatory frequency, and oscillatory amplitude were easily controlled via the Console and WaveMatrix software packages. Every test which was set under specified loading conditions lasted ten cycles and the data (i.e. force-displacement curves) in the last cycle were extracted and analyzed. By analyzing only the last cycle, we investigated the viscoelastic response at the steady state and not in the transient regime. In addition, the quasi-static compressive properties of the layered polymeric composites were measured by an Instron 5882 electromechanical testing machine (load capacity: $\pm 100 \text{ kN}$). The analyzing methods for nonlinear viscoelasticity (i.e. Fourier transform and geometrical nonlinear analysis) based on the experimental data and the definitions of related parameters (such as Fourier intensities I_n/I_1 , compressive stiffness E_M and E_L , and geometrical nonlinear parameter S) are introduced in Supporting Information in detail.

3. Results and Discussion

3.1 Nonlinear viscoelasticity under different loading conditions

Nonlinearity in viscoelastic composites is closely related to the loading condition. In this section, we discuss the influence of pre-compression, oscillatory frequency, and oscillatory amplitude on the viscoelasticity of layered structural composites under LAOC. Unless otherwise noted, we use results from the 9 layered polymeric composite with the same volume fraction of hard polymer and soft polymer for the discussion.

In complex fluids, the residual force can be ignored under quasi-static loading. However, pre-compression is needed in viscoelastic solids under oscillatory compression to make sure that the loading plate contacts the upper surface of the sample during the test. This creates a static force induced by the pre-compression that is superimposed on the response force under oscillatory compression, as shown in Fig. 1. Here, we ensure that the static force corresponds to a steady-state relaxed configuration by maintaining the pre-compression for a long enough time (10 min) before the dynamic mechanical test.

By keeping the oscillatory frequency and the oscillatory amplitude constant, we can probe the effect of pre-compression on nonlinear viscoelasticity. The initial offset of the response force at the beginning shown in Fig. 2a corresponds to the static force. Flat curves occur in Fig. 2a when the value of pre-compression is close to the oscillatory amplitude. However, the force in this area does not drop to zero. We can therefore safely confirm that the loading plate and the sample did not separate during the test and that the experimental results are reliable. The stiffness of the soft polymer was about three orders of magnitude less than the stiffness of the hard one, which implies that the deformation mainly initially occurs in the soft polymeric layer when the response force is very small. The quasi-static compressive curve of the 9 layered polymeric composite shown in Fig. S2 is consistent with this result. The initial flatness of the curve is therefore mainly from the large deformation of the soft polymer. As the pre-compression increases, the constraint between the hard layer and the soft layer also increases, causing the whole sample to deform coordinately and the flat

curve to disappear gradually.

Fig. 2 Time-dependent response force during one loading cycle of 9 layered polymeric composite with different pre-compression loads (oscillatory frequency : 0.1 rad/s; oscillatory amplitude: 0.02mm) (a); Relationship between relative Fourier intensity (I_n/I_1) and relative angular frequency (ω/ω_1) in the frequency domain (b); The first 20 relative Fourier intensities (I_n/I_1) under the specified loading conditions (the same result is plotted on log coordinates, as shown in the inset) (c); I_2/I_1 under different oscillatory frequencies as a function of pre-compression (d).

The force distortion (a non-standard sinusoidal force curve in response to the single-harmonic sinusoidal displacement stimulus) indicates nonlinearity. We used FT to quantitatively characterize this nonlinearity in the frequency domain. Fig. 2b shows the first 200 relative Fourier intensities (I_n/I_1 , definition can be found in supporting information) calculated from Fig. 2a. The relative Fourier intensity (I_n/I_1) decreases quickly at first and then trends to stabilize (the transition point of relative angular frequency (ω/ω_1) is about 20). The Fourier intensity in the plateau region is mainly induced by noise and can be ignored [28, 34]. We then plotted the first 20 relative Fourier intensities (I_n/I_1) under the specified loading condition (as shown in Fig. 2c) as linear and log coordinates. It is very clear that the second-order term dominates the nonlinearity (Fig. 2c) and that the second relative Fourier intensity (I_2/I_1) captures the degree of nonlinear viscoelasticity of layered polymeric composite under LAOC, which is quite different from what occurs in FTR. The second to fifth relative Fourier intensities are comparable for complex fluids under large amplitude

oscillatory squeeze (LAOSQ) [47], so I_2/I_1 cannot be directly used for describing nonlinear viscoelasticity in this situation. If the dynamic mechanical response of complex fluids is obtained under LAOS, I_3/I_1 is usually used as the nonlinear parameter due to the odd-symmetry of Lissajous curve [38]. Fernandes *et al* defined linear viscoelastic limit of complex fluids as $I_3/I_1=0.5\%$ [40]. For viscoelastic solids, the value of I_2/I_1 determines the degree of nonlinear viscoelasticity (Fig. 2c), so here we define a limit of linear viscoelasticity as $I_2/I_1=0.3\%$ based on the experimental results shown in Fig. 2d.

With this definition, we next calculated I_2/I_1 with different pre-compression and frequencies, as shown in Fig. 2d. As the pre-compression increased, I_2/I_1 decreases accordingly, indicating that the layered polymeric composite tends to be linear viscoelastic. In Fig. S2, three deformation regions are defined based on the compressive curves of the 9 layered polymeric composite. The sample approximately linearly deforms within the respective deformation region, but the mechanical behaviors are quite different if the material is compressed from one deformation region to another one. Fig. 2a also indicates that a similar deformation mechanism is applicable for dynamic mechanical test. If the difference between the pre-compression and the oscillatory amplitude is smaller than 0.08mm (i.e. $u_0 - \Delta u \leq 0.08 \text{ mm}$), nonlinear mechanical behavior appears, and this nonlinearity can be further quantitatively characterized by I_2/I_1 (Fig. 2d). In addition, it is easy for the layered polymeric composite to move into the linear viscoelastic range under lower frequency: the critical pre-compression value for moving into the linear viscoelastic range at 0.025 rad/s is about 0.06 mm while the material falls into the linear viscoelastic range when the pre-compression is 0.10 mm at 1.0 rad/s. This frequency-dependent nonlinear viscoelasticity originates from the stress relaxation of the layered polymeric composite and can be ignored if a lower oscillatory frequency is chosen. In addition, the inertia effect and interfacial slip should be considered if a high oscillatory frequency is applied [44]. However,

these effects are beyond the scope of this paper, we therefore chose a small oscillatory frequency (0.01Hz) in our most tests.

Fig.3 Geometrical nonlinear analysis of 9 layered polymeric composite with different pre-compression and oscillatory frequencies (the oscillatory amplitude is 0.02mm).

We also calculated another parameter to evaluate the nonlinear viscoelasticity of layered polymeric composite by using geometrical nonlinear analysis, as shown in Fig. 3. The dimensionless parameter S (definition can be found in supporting information) can reflect the nonlinear status in both loading and unloading stages. Similarly, if S tends toward zero, the material is linear viscoelastic. A similar tendency of S in the unloading stage in comparison with I_2/I_1 can be found, indicating that the nonlinear viscoelasticity of a layered polymeric composite can also be quantitatively characterized by S . Moreover, the asymmetry of the response force (or the Lissajous curve) can be clearly distinguished by the different values and tendencies of S when varying with the pre-compression and oscillatory frequency in the loading and unloading stages (Fig. 4). We found that the layered polymeric composite in the loading stage is strain stiffening (all S are positive) while in the unloading stage the layered polymeric composite is strain softening (all S are negative).

Fig. 4 The time-dependent response force during one loading cycle 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). Relationship between I_2/I_1 and oscillatory amplitude with different pre-compression (d).

The oscillatory amplitude-dependent dynamic modulus (G' or G'') is an important indicator of the linear viscoelastic range in dynamic mechanical analysis (DMA) tests. In the NVE range, the influence of the oscillatory amplitude on nonlinear viscoelasticity can be analyzed at fixed oscillatory frequency and pre-compression, as shown in Fig. 4a, 4b, and 4c. Flat curves appear again when the oscillatory amplitude is close to the value of pre-compression (Fig. 4a and 4b). Corresponding Lissajous curves (Fig. S3a and S3b) are quite similar with the cyclic curves obtained in quasi-static compressive tests (Fig. S2), suggesting the above-mentioned deformation mechanism can be used to explain this result. When the pre-compression is set at 0.20 mm, the flat curve disappears because $u - \Delta u \geq 0.10$ mm (i.e. the material is compressed in the coordinated deformation region during the whole test). However, the Lissajous curves are not elliptical (Fig. S3c) even without force distortion (flat curve in the unloading stage), indicating another kind of nonlinear mechanism exist in the coordinated deformation region.

The two nonlinearities observed in our results can be clearly distinguished by I_2/I_1 as shown in Fig. 4d. On the one hand, the force distortion can be detected by I_2/I_1 . Once the flat

curve appears (the sample is compressed from one deformation region to another), I_2/I_1 with 0.08 mm and 0.14 mm pre-compression increased significantly. Moreover, the degree of distortion is also reflected in I_2/I_1 (the value of I_2/I_1 with 0.08 mm pre-compression is larger than that of I_2/I_1 with 0.14 mm pre-compression). On the other hand, I_2/I_1 with 0.20 mm pre-compression is not close to 0.3% and linearly increases with increasing oscillatory amplitude (Fig. 4d). This kind of nonlinearity is induced by the hard and soft polymers themselves (complex movement of polymer chains inside the material on the molecular scale) and the coordinated deformation between different polymeric layers.

Fig. 5 Geometrical nonlinear analysis of layered polymeric composite with different pre-compression and oscillatory amplitude (oscillatory frequency is 0.01 Hz).

Further, we found that S in the loading stage linearly increases with increasing oscillatory amplitude and is much smaller than that in the unloading stage (Fig. 5), which suggests that the nonlinear viscoelasticity induced by coordinated deformation originates in the loading stage and the raw polymers, no matter how much pre-compression there is. In addition, the nonlinearity originating from flat curves only appears in the unloading stage (a remarkable increase of S can be observed, similar to I_2/I_1 , as shown in Fig. 5), which is consistent with the experimental results (Figs. 4a, 4b, and 4c). These results demonstrate that the nonlinear mechanism can be further subdivided by S . Similarly, the material characteristics (strain stiffening or strain softening) of layered polymeric composites can be

clearly identified through the sign (positive or negative) of S .

Fig. 6 I_2/I_1 of 9 layered polymeric composite as a function of oscillatory amplitude at different oscillatory frequencies (the pre-compression is set at 0.20 mm) (a); Contour map of nonlinear viscoelasticity for 9 layered polymeric composite (each color on the color bar indicates different values of I_2/I_1 . In other words, different colors represent different nonlinear viscoelasticity) (b).

Oscillatory frequency is another important parameter that controls the dynamic loading condition. Fig. 6a shows I_2/I_1 of a layered polymeric composite under different oscillatory amplitudes and oscillatory frequencies. A linear relationship between I_2/I_1 and oscillatory amplitude at different oscillatory frequencies is evident. Similar linear relationship also reported for polymer melt under LAOS [35, 41, 53] and LAOSQ [47]. The difference is that the slope of I_2/I_1 for the polymer melt at different frequencies is same [41], whereas the slope of I_2/I_1 for the layered polymeric composite decreases gradually with increasing oscillatory frequency (Fig. 6a). That is, the viscoelasticity of the layered polymeric composite tends to being linear under high frequency. The data shown in Fig. 6a can be alternately drawn as a contour map (also called as Pipkin diagram), as shown in Fig. 6b. This contour map also indicates the variation in the nonlinear viscoelasticity with two independent parameters [32]. The navy-blue region signifies that the material is linear viscoelastic while the material tends to be nonlinear viscoelastic if the loading condition is located in the red region.

3.2 Nonlinear viscoelasticity of layered polymer composite with different inner structure

The loading condition is not the only way to determine the nonlinear viscoelasticity of a layered polymeric composite. The inner structure of the composite can also determine the nonlinear viscoelasticity. The inner structure of a layered structural composite is described by

the volume ratio between the hard and soft polymers and the number of layers. In this section, we first compare the nonlinear viscoelasticity of raw polymers and a 9 layered polymeric composite made from raw polymers given that the geometry of the raw polymer is the same as that of the layered polymeric composite. We then discuss the nonlinear viscoelasticity of layered polymeric composites with different inner structures. The soft and hard polymers can be regarded as polymeric composites with 0% and 100% of volume fraction of hard polymer, respectively.

Fig. 7 Time-dependent response force during one loading cycle of soft polymer (a), 9 layered polymeric composite (b), and hard polymer (c) at different oscillatory amplitudes. Oscillatory frequency: 0.01 Hz; Pre-compression: 0.20 mm. I_2/I_1 of different materials as a function of oscillatory amplitude (d).

Fig. 8 Geometrical nonlinear analysis of different materials at different oscillatory amplitudes.

As expected, the dynamic response force (Figs. 7a, 7b, and 7c) and the quasi-static

stiffness (Fig. S4) of 9 layered polymer composite is between the soft and hard polymer under the same loading condition. These results are consistent with what would be expected from homogenization bounds. However, the nonlinear viscoelasticity does not follow this rule: I_2/I_1 of the 9 layered polymeric composite is much larger than that of soft or hard polymer, as shown in Fig. 7d. We therefore conclude that structuration (here mainly layering) is one of the effective ways to create nonlinear viscoelasticity. The internal strain in the layered polymer composite is more complicated than that in the raw material and this complicated stress environment may be the source of nonlinearity. Force distortion (i.e. flat curves in the unloading stage) is observed in Fig. 7c at large oscillatory amplitudes. All of the forces in the flat curves are equal to zero. These observations differ from the results reported in Fig. 2a, Figs. 4a and 4b. This observation suggests that plastic deformation occurs (we did not find an obvious crack on the hard polymer after compression) if the compressive strain exceeds a critical value in the dynamic loading condition, and this critical compressive strain is between 6.75% and 7%. Force distortion is still well captured by I_2/I_1 (Fig. 7d), but the nonlinear mechanism is different in this case. From the results obtained from the geometrical nonlinear analysis (Fig. 8), we know that the S of soft polymer is close to zero all the time and the S of hard polymer is negative even in the loading stage. These results demonstrate that the soft polymer is linear viscoelastic even with a relatively large oscillatory amplitude while the hard polymer is always strain softening.

Further, we compared the nonlinear viscoelasticity of 9 layered polymeric composite with different volume ratios with the nonlinear viscoelastic parameter I_2/I_1 (Fig. 9a) and S (Figs. 9b and 9c). For convenience of the discussion, data on the soft and hard polymers are also included. Interestingly, I_2/I_1 increases with the increasing volume ratio of the hard polymer at first. It then decreases with the further increasing volume ratio of the hard polymer. The maximum I_2/I_1 appears in the 9 layered polymeric composite with the equal

volume fraction as hard polymer and soft polymer no matter what the oscillatory amplitude is (Fig. 9a). The only exception is the large I_2/I_1 of hard polymer (100% volume fraction of hard polymer in Fig. 9a) at a large oscillatory amplitude. This is attributed to the distortion of the response force curves (see Fig. 9c), which we discussed above. A similar tendency can also be found in the volume ratio-dependent S at the loading stage, as shown in Fig. 9b. However, it seems that there is no obvious regularity for the volume ratio-dependent S at the unloading stage (Fig. 9c).

Fig. 9 I_2/I_1 of 9 layered polymeric composite with different volume ratios at different oscillatory amplitudes (a); Geometrical nonlinear analysis of 9 layered polymeric composite with different volume ratios at loading (b) and unloading (c) stages. Tangent stiffness E_M , secant stiffness E_L , and quasi-static compressive stiffness E_C of 9 layered polymeric composite with different volume ratios at different loading stages. E_M and E_L are average value with error bar at different oscillatory amplitude (d); Oscillatory frequency: 0.01 Hz; Pre-compression: 0.20 mm.

Fig. 10 I_2/I_1 and geometrical nonlinear analysis of the layered polymeric composite with different layer numbers at different oscillatory amplitudes. Oscillatory frequency: 0.01 Hz; Pre-compression: 0.20 mm.

Although the geometrical nonlinear analysis is based on the dynamic compressive stiffness (E_M and E_L), the variations of compressive stiffness and S with volume fraction of hard polymer are quite different. When the volume fraction of the hard polymer increases, the compressive stiffness (E_M , E_L , and E_C) increases gradually (Fig. 9d). In addition, the dynamic compressive stiffness (E_M or E_L) is always larger than the quasi-static compressive stiffness (E_C , measured under the same condition as illustrated in Fig. S2). These results indicate that nonlinear viscoelasticity is not directly determined by the mechanical properties of layered polymeric composite. The inner structure and the constraint between soft and hard layers may be the source of nonlinear viscoelasticity. According to the experimental results shown in Figs. 9a and 9b, we can speculate that the polymeric composite with small gap of volume fraction between the hard and soft polymers tends to generate large nonlinear viscoelasticity due to the strong constraint between hard and soft polymers. In other words, the inner structure of the layered polymeric composite with different composition (the volume fraction interval of hard polymer is 0~0.5 or 0.5~1) can be distinguished by nonlinear viscoelastic parameters (i.e. I_2/I_1 and S at the loading stage). The deformation regions and the transition point between different deformation regions change with the variation of volume ratio and they are sensitive to the experimental conditions. The nonlinear viscoelasticity is therefore different under the same unloading condition for the layered polymeric composite with different volume ratios (Fig. 9c).

The mechanical properties of layered polymeric composites were found to be effectively enhanced by increasing its number of layers with a fixed composition [54]. We drew a similar conclusion in this study. Fig. S4a shows that the stiffness of the layered polymeric composite increases with the increasing number of layers. However, it seems that the number of layers has no significant influence on the nonlinear viscoelasticity. The nonlinear parameters (I_2/I_1 and S) cannot well distinguish the layered polymeric composite

with different number of layers (Figs. 10a and 10b). Although the samples in the part of the study had different number of layers, the composition of the polymeric composite remained fixed (the volume ratio of soft and hard polymers remained 1:1). This means that the deformation regions in the specified loading conditions do not change a lot, like the compressive curve shown in Fig. S2. As we discussed above, nonlinear viscoelasticity is mainly determined by the range of deformation regions if there is no force distortion. Thus, the nonlinear parameters for the layered polymeric composite with specific layer numbers (5, 7, and 9 layers) remain very close. In the 11 layered polymeric composite, an obvious force distortion was observed (see Fig. S5), which may be induced by the extrusion of soft polymer (Fig. S6b) and delamination of hard polymer (Fig. S6c), not due to transitions between deformation regions (Fig. 2a, Figs. 4a and 4b). As the number of layers increases, the thickness of each layer becomes thinner, indicating that the constraint between the hard and the soft polymer is strengthened. The stiffness can be effectively increased by the constraint. Meanwhile, a strong constraint makes the layered polymeric composite more prone to damage. Therefore, the structure of the 11 layered polymeric composite breaks during the dynamic mechanical test when the oscillatory amplitude exceeds to 0.06 mm. This structure collapse is clearly captured by nonlinear parameters (I_2/I_1 and S). It is need to note that the structure collapse may start from the micro-cracks inside the sample before the extrusion of soft polymer and the delamination of hard polymer occur.

Fig. 11 Dissipated energy (a) and the normalized dissipated energy at different loading stages (b) of the layered

polymeric composite with different layer number as a function of oscillatory amplitude.

Dissipated energy during a loading cycle is another important characterization parameter in dynamic mechanical tests. We compared the dissipated energy of various layered polymeric composites and found that the dissipated energy increases as the number of layers increases (Fig. 11a), following the same tendency of the dissipated energy under quasi-static cyclic compression (Fig. S4b). We also calculated the dissipated energy during different loading stages (see Fig. S1b) and their proportion to the total dissipated energy (Fig. 11b). The normalized dissipated energy is an indicator of the asymmetry of the Lissajous curve (In linear viscoelastic range, Lissajous curve trends to be elliptical, which indicates that the normalized dissipated energies in the loading and unloading stages should be close to 0.5, such as the starting points in Fig. 11b). As the oscillatory amplitude increases, a greater proportion of energy is dissipated during the loading stage, indicating increasing nonlinear viscoelasticity. This is consistent with the results obtained from FT (Fig. 10a) and geometrical nonlinear analysis (Fig. 10b). Moreover, the layered polymeric composite with a large number of layers tends to dissipate more energy in the loading stage (Fig. 11b). From this point of view, the dissipated energy not only characterizes the nonlinear viscoelasticity, but also identifies the inner structure (i.e. layer number) of the layered polymeric composite.

4. Conclusion

In summary, here, we investigated the nonlinear viscoelasticity of pre-compressed layered structural composites under large amplitude oscillatory compression (LAOC). Fourier transform and geometrical nonlinear analysis, methods first developed in rheology, were introduced to quantitatively characterize nonlinear viscoelasticity in these layered polymeric composites. Our results indicated that both methods are effective in analyzing the asymmetric dynamic mechanical behaviors of viscoelastic solids. The nonlinear viscoelasticity characterized by these methods results from stress relaxation of raw polymers, the loading condition (including pre-compression, oscillatory frequency, and oscillatory

amplitude), and changes in the inner structure of the layered polymeric composite. Further analysis demonstrated that nonlinear viscoelasticity is essentially attributed to the change in the inner structure (transition between different deformation regions, cracking of polymer components), and these changes can be induced by the loading condition. The characterization methods presented in this work therefore are not only helpful for deep understanding of the nonlinear viscoelastic mechanism but they are also valuable for optimizing the inner structures of structural polymeric composites.

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