WHY IS THE PYANE EFFECT MISSING HIGHER HARMONICS?

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ABSTRACT

Rubbers filled with a large amount of nanosized particles, such as carbon black (CB) or silica, often display a very unusual nonlinear behaviour under large-amplitude oscillatory shear (LAOS), where the amplitude stress strongly deviates from the linear dependence of strain while the time dependence of stress remains sinusoid. This unusual sinusoidal responses of filled rubbers, however, should not be confused with the fact that the rubbers are highly nonlinear viscoelastic materials as seen in typical stress-strain curves. In our recent studies, we have referred to this phenomenon as the "linear-nonlinear dichotomy" [1-7] of the Payne effect of filled rubbers. In order to understand the molecular details regarding this unusual behaviour, we chose a system with only three basic ingredients: polymer, filler, and oil. By changing the filler content and particle size, and by studying the matrix of various polymer concentrations and molecular weights, we have observed the impacts of the filler particle size, the filler loading, and the matrix composition on this very unusual rheological behaviour. A summary of our research activities on this subject in Tongji will be presented.

LINEAR-NONLINEAR DICHOTOMY RHEOLOGY

What we mean by this terminology is that the unusual nonlinear behaviour of filled rubber under oscillatory shear consists of two seemingly contradictory parts. The dynamic behaviour is nonlinear in the sense that the storage and loss moduli depend strongly on the strain amplitude, while the stress response appears to be linear because that at each of the strain amplitudes it is simply a sinusoidal offset from the oscillatory strain input (or vice versa). Mathematically, this "dichotomy" nonlinear phenomenon can be described by the following expression:

$$\sigma(t,\gamma_0) = \gamma_0 \left[G'(\gamma_0,\omega) \sin(\omega t) + G''(\gamma_0,\omega) \cos(\omega t) \right] \tag{1}$$

where the input strain γ varies as $\gamma = \gamma_0 \sin(\omega t)$, γ_0 is the strain amplitude and ω is the angular frequency. Equation (1) exhibits the "linear-nonlinear dichotomy" characteristics. It is a linear viscoelastic equation that predicts perfect sinusoidal waves when γ_0 is constant, otherwise it is a nonlinear viscoelastic equation if γ_0 is a variable. Of course, equation (1) simplifies the actual situation of the nonlinear responses of real materials because it is a first-order approximation of the Fourier series. This simplification occurs in many physics. One such example is the ideal gas law as the first approximation that helps us model and predict the behaviour of real gases.

Therefore, the concept of "linear-nonlinear dichotomy" represents an ideal state in the rheological sense. There is no material that behaves exactly ideally, but there are plenty of filled rubber compounds that behave so closely that the concept of an ideal "dichotomy" state is an extremely useful approximation for many situations.[3,4] Fourier transform analysis shows that in many investigations of filled rubbers [1-7] higher-order harmonics of a filled rubber can sometimes be detected by a sensitive rheometer, but they are usually very small and negligible. The ratio of the third to the first harmonic responses (I_3/I_1) in the range when G'' passes through its maximum is typically less than 3%, and sometimes even less than 1%.[2]

As a result, the storage and loss moduli of a filled rubber in the nonlinear regime are still well defined by the first-order harmonic response functions. The standard deconvolution of experimental torque and phase offset in terms of the first harmonics G' and G'' is still appropriate at each strain amplitude in the nonlinear regime. The relationships between the dynamic moduli and the average energies stored and dissipated per cycle per unit volume and their physical meaning are still applicable in the nonlinear regime of a filled rubber due to what we call this ''the linear–nonlinear dichotomy'' of these materials. This unique feature of filled rubbers has been widely used by engineers and compounders in compound designs, characterizations and applications in rubber industries. Tires provide quiet and comfortable driving, due in part to the quasi-sinusoidal responses of tread rubbers to cyclic deformations. Despite the technological significance of the linear–nonlinear dichotomy phenomenon, the root cause for this peculiar "dichotomy" behaviour of filled rubbers has been a long-term puzzle.

THE LASTEST DISCOVERIES

Recently, it was found that particle-filled polymer melts of widely varied molecular weights exhibit a rheological transition [5] as the molecular weight of the matrix, M_n, increases and passes through a characteristic molecular weight M_c^*. Below M_c^*, the system shows typically the classic nonlinearity, where the storage modulus G' decreases as the strain amplitude γ_0 increases and the resulting stress waveforms are distorted from sinusoidal waves. Above M_c^*, the system displays a new nonlinearity, where the stress responses at any given strain amplitude remain surprisingly sinusoidal regardless the drop of modulus G'. The critical point M_c^* is found to be a few times of the entanglement molecular weight M_e.

In addition, it was also observed that particle-filled polymer solutions with wide changes in their compositions display a similar rheological transition [6] as the matrix polymer concentration ϕ approaches and passes through a critical value ϕ_c. Below ϕ_c, the system shows the classic viscoelastic nonlinearity, where the storage modulus G' decreases as strain amplitude γ_0 increases and the deviation of the stress signal from a sinusoidal wave is significant. Above ϕ_c, however, the system displays an anomalous nonlinearity, where the ratio of the third to the first harmonic responses I_3/I_1 of the stress signal is negligibly small and essentially independent of the drop in modulus G', and the system actually shows the quasi-sinusoidal responses in the nonlinear regime. The transition to linear-nonlinear dichotomy takes place in the concentrated polymer solutions where the polymer chains are highly entangled.

Furthermore, it was discovered [7] that this transition is insensitive to the strain amplitude, G'/G'_0, and filler loading but is very sensitive to the filler particle size d. Increasing the filler particle

size significantly decreases the critical ϕ. However, increasing the filler loading basically has no effect on the transition to linear-nonlinear dichotomy. This transition is detectable under either fixed strain amplitudes or fixed G''/G'_0 conditions, and happens when the mesh size ξ of the entangled polymer network in the matrix becomes smaller than the primary filler particle size d.

CONCLUSIONS

The degree of entanglements in polymer chains seems to play a key role in the linear-nonlinear dichotomy rheology. The time scale for topological rearrangements of entangled polymer chains that affect particle motion in the matrix is the crucial factor, and depends on polymer molecular weight, concentration and temperature. As the polymer concentration ϕ approaches and passes through ϕ_c, the filler particles may experience a sudden local blockage of their movements due to the topological hindrance of the entangled polymer chains. The sinusoidal stress response of the material in the nonlinear region is due to a sudden blockage of the filler particle movement when the polymer chains are entangled, and the entanglement mesh size ξ decreases to below the filler particle size d.

IMPLICATIONS

This "linear-nonlinear dichotomy" feature in the nonlinear rheological responses of filled rubbers can directly lead to a much general perspective, i.e., the frequency-deformation separability principle.[3] Thus, the measured dynamical properties can be separated into a linear viscoelastic frequency-dependent part and a nonlinear strain-dependent part, which can directly lead to other superposed behaviours for measured properties. In addition, when the higher order harmonics are negligible, the damping function in static relaxation is equivalent to the Payne effect in oscillatory shear.[4] This equivalence can phenomenologically link the linear and nonlinear properties of filled rubbers and has important implementations.

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