

Filled Rubbers Manifesting Superposed Nonlinear Viscoelasticity

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ABSTRACT

Seeking relations for inter-conversions of viscoelastic properties of rubber materials in the nonlinear regime is a scientifically challenging and industrial important problem. In this study, responses of vulcanized filled rubbers to step shears and oscillatory shears are investigated. In both linear and nonlinear regimes the mechanical properties of the filled rubbers exhibit excellent superposed rheological behaviour. The damping function derived from the stress relaxations is found to be equivalent to the Payne effect obtained from the frequency-strain superposition. The implication of this result will be discussed.

INTRODUCTION

Rubbers filled with carbon black and silica can be processed to meet various requirements and have been adopted by industries for numerous applications, including gaskets, damping materials, transport belts, and automobile tires. Typical stresses and strains in these applications place the behaviour of rubbers right in the middle of their nonlinear regime. Whereas the phenomenological theory of linear viscoelasticity of rubbers is well established¹, the subject of the nonlinear viscoelasticity of filled elastomers has not reached a similarly advanced state. For nonlinear viscoelasticity, relations for inter-conversions of the functions of modulus and

compliance are generally unknown². At present, nonlinear properties of rubbers such as stress-strain, creep compliance, and dynamic moduli are independently characterized and measured in rubber industries. Therefore, searching for a universal description of the nonlinearity in filled elastomers and seeking an effective way to construct master curves that may link together the linear and nonlinear properties have important implementations.

EXPERIMENT

In this work, vulcanized filled rubber compounds with generic compositions were prepared in close accordance with ASTM D 3184. A 340-gram rubber compound was formed by mixing 100 parts per hundred rubber (phr) of polymer, 20-80 phr N330 carbon black, 4 phr zinc oxide, 1.5 phr N-sec-octyl-N'-phenyl-p-phenylene diamine (antioxidant), 1 phr stearic acid, and 1 phr wax in a Brabender mixer at 110°C and 60 rpm for 4 min to form a master batch stock. To form a final stock, the rubber stock was remixed with curatives in the same mixer at 70°C for 1.5 min. The curatives incorporated were 1.8 phr sulfur, 1.5 phr N-cyclohexyl-2-benzothiazole sulfonamide (accelerator), and 0.4 phr tetramethyl thiuram monosulfide (accelerator).

The gum polymer used was a poly(styrene-co-butadiene) or SBR rubber. The rubber was a commercial SBR-1502 from PetroChina. The polymer has $M_w =$

440 kg/mol, $M_w/M_n = 3.40$, 23.5 wt % randomized styrene, and the following butadiene unit structures: 10% cis-1,4, 69% trans-1,4, and 21% 1,2-vinyl additions. The glass transition temperature of the polymer is about -47°C . The Mooney viscosity of the polymer is approximately 50 at 100°C . Carbon black (N330) was employed in this investigation for its all-purpose reinforcement. Filler loading varied from 12 to 28% by volume fraction.

Mechanical measurements were carried out using an ARES-G2 strain-controlled rheometer with a torque range from 0.05 μNm to 200 mNm. This equipment was controlled by a PC with the standard TRIOS V4.0 software. This rheometer were from the TA instrument. A ring sample with inner and outer diameters of about 14.5 mm and 15.8 mm, respectively, was cut from the cured rubber slab of thickness of about 3.5 mm. The ring cutter assembly and the cutting procedure were in close accordance with ASTM D412. The rubber ring was then glued in a concentric manner between a pair of parallel plates using superglue. A thin layer of few μm thick of the cyanoacrylate-based glue was used to attach the sample to the two plates. To ensure the sample ring was concentric in the parallel plate fixture, we designed a cylindrical tool mounted on the rheometer that can centre and release the ring into the proper position³.

NONLINEARITY UNDER STEP-SHEAR

Fillers such as carbon black or silica are commonly added to commercial elastomers for reasons of economy and for favourably modifying the properties such as improved abrasion, tear, cutting and rupture resistances. However, due to filler agglomeration, the effect of reinforcing fillers on the modulus is very strain dependent. When the step-shear strain is sufficiently small, the modulus of a rubber is independent of the strain. Up to about 0.3% strain, the relaxation modulus remains the

same (as shown in Fig. 1). As the strain is increased beyond 0.3%, the relaxation modulus become strain-dependent and decreases with increasing applied strain. Although the magnitude of the relaxation modulus decreases, all experimental curves display remarkable similarity with the increase of time and constantly shift along the vertical direction with the increase of strain. According to this observation, the relaxation stress σ can be factorized into a strain dependent part and a time dependent part:

$$\sigma(t, \gamma) = \gamma G(t, \gamma) = \gamma h(\gamma) G(t) \quad (1)$$

where $G(t)$ is the stress-relaxation modulus in the linear regime as function of the time t and the strain dependent part, $h(\gamma)$, is the so-called damping function⁴ (see Fig. 2).

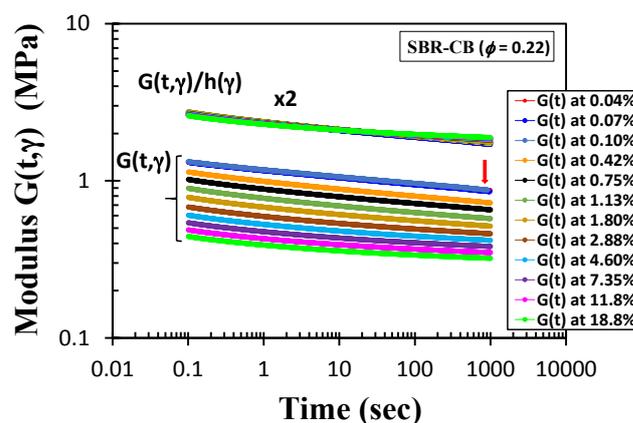


Fig. 1. Relaxation modulus $G(t)$ versus time t at various strains at 25°C for the SBR-CB rubber.

Attempt to establish rheological constitutive equations in agreement with this law of time-strain factorization by generalization of the Boltzmann's theory of time-elastic processes has drawn much attention in the past. Among them, the K-BKZ integral constitutive equation has shown the most success in predicting the behaviour of polymer melts and particle-suspended soft materials in complex flows

and deformations of scientific and industrial importance and has led significant influences in the rheological community. The concept of the damping function has been examined in numerous different systems⁴, including polymer composites, liquid crystals, polymer blends, suspensions, emulsions, micellar systems, and in food rheology. Various expressions for the damping function have been proposed in order to achieve a better fit for the experimental data⁴, for instance, the exponential decay function, the sigmoidal function and the modified sigmoidal formula. Nevertheless, the most important thing is that Eq. (1) has been experimentally proved to be valid for many polymers, solutions and particle-filled systems.

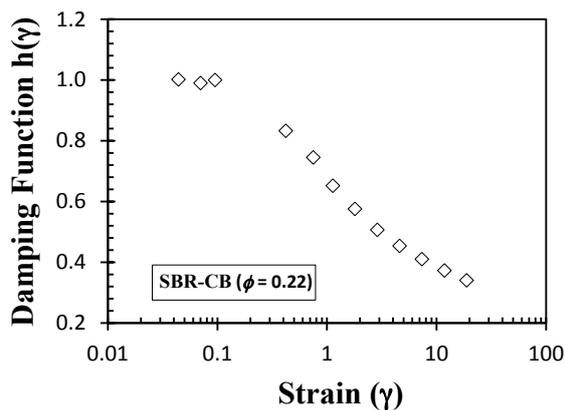


Fig. 2. Damping function obtained from the stress relaxations shown in Fig. 1.

NONLINEARITY UNDER OSCILLATORY-SHEAR

It is interesting to note that under oscillatory shearing conditions the storage modulus G' of a filled rubber also decreases with the increase of the strain amplitude γ . This behaviour apparently is frequency-insensitive. As can be seen in Fig. 3, the linear range for the dynamic moduli is very small and the deflection for G' happens at a strain $\gamma_y < 0.1\%$. The drop in G' is large, and the modulus G' loses 75% of its original value by about 10% strain deformation. This drop is accompanied by a maximum of the

loss modulus G'' . At sufficiently large strain amplitudes (roughly 20%), the storage modulus approaches a lower bound. This phenomenon of filled rubbers is often called the Payne effect⁵ and has important industrial implementations. Typical dynamic stress and strain in many applications place the behaviour of rubber right in the middle of the nonlinearity.

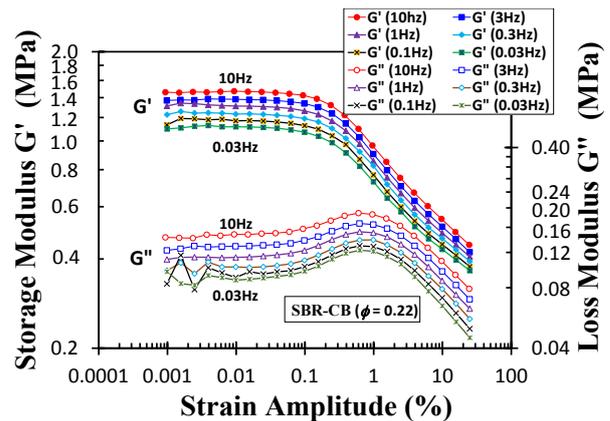


Fig. 3. G' and G'' at 25°C versus γ_0 for the SBR-CB rubber at various frequencies.

It should be noted that although disruption of the agglomerated particles and particle network in the rubber matrix introduces strong nonlinearities into the dynamic mechanical behaviour of the filled rubber compound, the response of these materials to the forced oscillatory shear at any given strain still remains surprisingly linear and sinusoidal⁶. Therefore, the standard deconvolution of the experimental torque and phase offset in terms of G' and G'' is appropriate at each strain amplitude due to what we call the “linear–nonlinear dichotomy” of these materials, although the γ -dependent G' and G'' are not described by the standard linear viscoelastic expression (Boltzmann superposition) in terms of the relaxation modulus.

The observation of normal sinusoidal wave despite the strain-induced softening associated with the Payne effect type of viscoelastic nonlinearity of particle-filled

elastomers is not new. Rather it is a well understood feature of these materials, as shown in a recent review article by Heinrich and Kluppel⁸.

Increasing the frequency rises the values of G' and G'' . Although the frequency is varied over three orders of magnitudes, all experimental curves display constant shifts along the vertical direction with the increase of frequency. This behaviour can be seen in both linear and nonlinear regimes. This observation suggests that all experimental data for various frequencies can be collapsed onto a single master curve. This action can be accomplished by normalizing G' by G'_0 and G'' by G''_0 , where G'_0 and G''_0 are the zero-strain limited value of G' and G'' . The normalized results is shown in Fig. 4. Hence, the dynamic moduli (G' and G'') may also be separated into a strain dependent part and a frequency dependent part:

$$G'(\gamma_0, \omega) = f(\gamma_0) G'_0(\omega)$$

$$\text{and } G''(\gamma_0, \omega) = g(\gamma_0) G''_0(\omega) \quad (2)$$

where $G'_0(\omega)$ and $G''_0(\omega)$ are simply the linear viscoelastic relaxation moduli and the strain-amplitude dependent parts $f(\gamma_0)$ and $g(\gamma_0)$ are the nonlinear Payne effect.

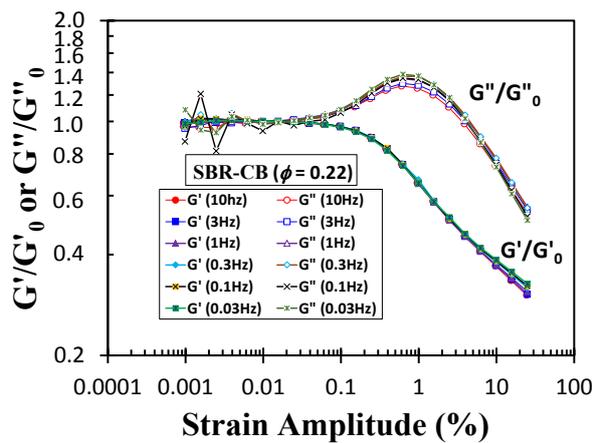


Fig. 4. Superposed nonlinear viscoelasticity

DAMPING FUNCTION AND PAYNE EFFECT

Since particle-filled rubbers in both step-shear and oscillatory-shear experiments display similar superposed rheological behaviour, the question now is whether the damping function $h(\gamma)$ obtained from the time-strain superposition takes the same function form as the Payne effect from the frequency-strain superposition? A comparison between the damping function and the Payne effect based on our experimental observations is depicted in Fig. 5. Remarkably, both sets of data appear to follow the same function of γ or γ_0 and surprisingly are overlapping each other, suggesting that the damping function obtained from the stress relaxations is equivalent to the real part of the Payne effect obtained from the frequency-strain superposition. This remarkable behaviour reveals the fundamental principles governing the nonlinear rheological behaviour of filled rubbers in both step-shear and oscillatory-shear conditions.

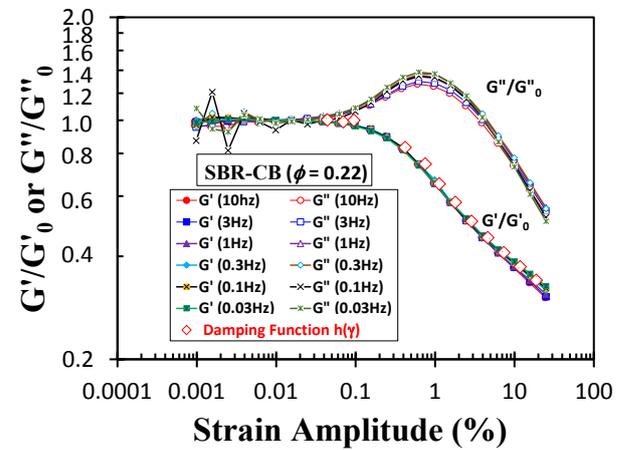


Fig. 5. Comparison between the damping function and the Payne effect for the SBR-CB rubber.

If the principle shown in Eq. (1) and the principle demonstrated in Eq. (2) are indeed coming from the same conjuncture in physics, we speculate that the Payne effect may be related to the damping function $h(\gamma)$

through a Fourier transformation of Eq. (1), such as

$$G^*(\omega, \gamma) = i\omega \int_0^\infty G(t) h(\gamma) e^{-i\omega t} dt \quad (3)$$

where G^* is the complex dynamic modulus. At an oscillatory strain $\gamma = \text{Re}(\gamma_0 e^{i\omega t})$, this relation will lead to generate two strain-dependent functions of $f(\gamma)$ and $g(\gamma)$ in the expression of the complex modulus G^* . One will be presented in the real part and the other will be shown in the imaginary part.

We do not become aware of any existing theoretical models trying to predict these functions through this route, but notice that the Kraus' expressions for the strain-dependence of f and g take following forms⁷:

$$f(\gamma) = \frac{1}{1 + (\gamma/\gamma_c)^{2m}}$$

and $g(\gamma) = \frac{2(\gamma/\gamma_c)^m}{1 + (\gamma/\gamma_c)^{2m}} \quad (4)$

where m and γ_c are model fitting parameters. A close inspection of them reveals that they have very similar forms to the sigmoidal function proposed by Papanastasiou *et al.*⁹ and by Soskey and Winter¹⁰. Hence, the relations of described (1) to (4) might phenomenologically link together the nonlinear stress relaxation and dynamic properties and thus have important applications for rubber materials.

CLOSE REMARKS

Up to now, we have investigated about a dozen of rubber compounds. The superposed nonlinear viscoelasticity is generally observed in all tested specimens, and is to a large extent independent of the filler content, the type of filler, the polymer used, and the compound preparation. The equivalence between the damping function and the Payne effect is surprising and

important. This linkage may designate the existence of natural laws in rubber mechanics that can be used to provide the important dynamics of a material over extended ranges of frequencies, strains, shear rates and temperatures. Recently, we have discovered that the law of frequency-deformation separability (or superposition) via a change of its independent variables can directly lead to a strain-rate frequency superposition¹¹, and shown that has important implementations that may link together the linear and nonlinear properties of rubber materials.

REFERENCES

1. Ferry, J.D. (1980), *Viscoelastic Properties of Polymers*, (John Wiley & Sons, New York).
2. Wang, Xr., and Robertson, C.G. (2005), "Strain-induced nonlinearity of filled rubbers," *Phys. Rev. E*, **72**, 031406.
3. Wang, Xr., and Robertson, C.G. (2010), "A New spectral memory of filled rubbers," *J. Polym. Sci.: Part B: Polym. Phys.*, **48**, 859–869.
4. Rolón-Garrido, V.H., and Wagner, M.H. (2009), "The damping function in rheology," *Rheol. Acta*, **48**, 245-284.
5. Payne, A.R. (1962), "The dynamic properties of carbon black-loaded natural rubber vulcanizates," *J. Appl. Polym. Sci.*, **6**, 57–63.
6. Robertson, C.G., and Wang Xr. (2006), "Spectral hole burning to probe the nature of unjamming (Payne effect) in particle-filled elastomers," *Europhys. Lett.*, **76**(2), 278-284.
7. Kraus, G.J. (1984), "Mechanical losses in carbon black filled rubbers," *J. Appl. Polym.*

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Sci.: Appl. Polym. Symp., **39**, 75–92.

8. Heinrich, G. and Klüppel, M. (2002), “Recent advances in the theory of filler networking in elastomers,” *Adv, Polym. Sci.*, **160**, 1–44.

9. Papanastasiou, A.C., Scriven, L.E. and Macosko, C.W.(1983), “An integral constitutive equation for mixed flows: viscoelastic characterization,” *J. Rheol.*, **27**(4), 387–410.

10. Soskey P.R., and Winter, H.H. (1984), “Large step shear strain experiments with parallel-disk rotational rheometers,” *J. Rheol.*, **28**(5), 625-645.

11. Li, S., Mi, Y., and Wang Xr. (2016) “Parallelism of nonlinear rheological behaviour manifesting in filled elastomers” ACS Spring Meeting, *PMSE-145*, San Diego. Also, a paper entitled “Superposed Nonlinear Rheological Behaviour in Filled Elastomers” submitted to *Journal of Rheology* (2016).