Nonlinear rheology of rubber materials

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INtROductIoN

Organic materials such as polymers and rubbers are characterised by (a) lightness and robustness, (b) a network structure, and (c) a time-dependent response. The first of these properties derives from the fact that string-like molecules of covalently bonded light elements randomly occupy space in such materials. The materials are never totally crystallised even when crystalline and cannot attain high density. Low specific gravity organic materials with this highly open structure have a low modulus of elasticity above the glass transition point. There are naturally times when they are used at high deformation: as would be expected, they experience large, rapid deformation in the course of mould processing. The reason they withstand large stimuli of this kind is the presence of networks in the material. Polymer materials only develop practical strength when the degree of polymerisation exceeds about 1000 [1]. Since the degree of polymerisation between entanglements is of the order of 100, the presence of intermolecular entanglements alone is insufficient – a network of entanglements must exist for practical strength to be displayed. The only reason crystalline polymers and block copolymers have strength is that that a pseudo-network structure exists in which the crystalline regions or high $T_g$ domains serve as a constraining phase [2, 3]. All dispersed nanofiller systems have some kind of network, be it due to polymer/polymer, polymer/filler or filler/filler interaction. Since networks due to interactions of different spatial scale thus underpin the materials, their mechanical properties too inevitably arise from a hierarchical structure; and being often physical in nature, these interactions are subject to nascence or extinction, which means that the mechanical properties of organic materials will be associated with structurally nonlinear systems. Obviously, since the structural unit is long, the materials cannot respond immediately to stimuli; time-dependence thus appears and viscoelasticity is exhibited. As these characteristics are extremely difficult to observe directly, we are compelled to observe them indirectly through stimulus-response relations, an area where rheology affords an extremely powerful tool. This article reviews the nonlinear viscoelasticity of carbon black (CB) filled rubber materials.

THE NONLINEAR VISCOELASTICITY OF FILLED RUBBER AND CAUTION IN DATA HANDLING

The viscoelasticity characteristics of filled rubber commonly manifest themselves in the strain amplitude dependence of the absolute dynamic elasticity modulus (the Payne effect [4-6]) as shown in Figure 1, and may be summarised by the following three observations. (1) At very low strain amplitude the modulus increases sharply with increasing filler content (filling effect); (2) the modulus decreases greatly with increase in strain amplitude (remarkable nonlinearity); and (3) the modulus at high strain amplitude in the filled system is of the same order as in the unfilled system (extinction of filling effect in the large deformation region). The nonlinearity of modulus in unfilled, uncured systems appears when the strain exceeds about 10%. As shown in Figure 2, this strain dependence corresponds with the linear-nonlinear transition strain [7] in polymer entanglement systems and it is thus clear that the nonlinear viscoelasticity of unfilled and uncured systems is due to the extinction of entanglements. However, the linear-nonlinear transition strain in uncured CB filled systems is far lower than the transition strain in unfilled and uncured systems. The
nonlinearity of CB filled systems is hence due to the filling effect.

The filling effect has been accounted for in two main ways: the filler gel hypothesis and the filler network hypothesis. It is true that a hard phase tightly bound to the filler exists around the filler particles [8]. However, the first hypothesis is unable to explain the aforementioned characteristics (2) and (3). The filler gel hypothesis would, if correct, mean that the gel phase starts transforming to sol at a strain of just a few percent and is wholly in sol form at a strain of about 100%, which is clearly unlikely. The characteristics are, on the other hand, readily explained from the filler network standpoint. The elastic modulus should increase if a filler network exists and decrease if part of the network is disrupted; moreover, if almost all the network is disrupted, the modulus should approach that of the unfilled rubber. The problem hence reduces to proving the existence of a filler network. Before taking the discussion further, we need to look briefly at the handling of nonlinear rheology data.

Papers presenting experimental results for the Payne effect are legion, and nearly all the results (to all intents and purposes that means all) are presented in the form of the strain amplitude dependence of the storage modulus $G'$ and loss modulus $G''$ as in Figure 3. In essence, however, the data ought to be presented in the form of the strain dependence of the absolute value of dynamic elasticity modulus as in Figure 1. The reason for this will be examined in more detail. As is well known, the dynamic modulus is defined by Equations (1) and (2):

$$G' = \frac{\sigma_{\text{peak}}}{\gamma_{\text{peak}}} \cos \delta$$

$$G'' = \frac{\sigma_{\text{peak}}}{\gamma_{\text{peak}}} \sin \delta$$

where $\sigma_{\text{peak}}$ and $\gamma_{\text{peak}}$ are the peak value of the stress wave and peak value of the strain wave, respectively, and $\delta$ is the phase difference. Although at this point some will already be saying “Yes, we already knew that”, bear with me. The phase difference $\delta$ may be found by shifting the reduced stress wave, divided by the peak value, in parallel along the time axis until it overlies the reduced strain wave as shown in Figure 4a. Clearly, under a very small oscillation corresponding to linear conditions, the Lissajous figure will be an ellipse as in Figure 4b, and the phase difference can be uniquely determined. When the strain amplitude is increased, however, nonlinearity emerges as in Figure 4c, and while the stress wave is still a periodic wave, it is no longer a simple sine wave, and is impossible to superimpose on the strain wave despite being shifted parallel. Moreover, the Lissajous figure then departs from elliptical as in Figure 4d. It should thus be clear that, once nonlinearity has appeared, the phase difference $\delta$ between the stress and strain waves cannot be uniquely determined, and $G'$ and $G''$ are indeterminable. In practice, however, curves for $G'$ and $G''$ under large amplitude oscillating deformation are mysteriously displayed as in Figure 3. Let us try solving this riddle.

It is well known that any periodic function can be written as a superposition of sine or cosine functions of different frequency, i.e. as a Fourier series expansion.
The stress response wave for a sinusoidal strain of large amplitude \( \gamma_{\text{large}} \) and angular frequency \( \omega \) (Equation (3)) may be written as in Equation (4):

\[
\gamma = \gamma_{\text{large}} \sin \omega t 
\]

\[
\sigma = \sigma_1 \sin(\omega t + \delta_1) + \sigma_3 \sin(3\omega t + \delta_3) + \sigma_5 \sin(5\omega t + \delta_5) + \ldots \tag{4}
\]

where \( \sigma_1 \) and \( \delta_1 \) are respectively the amplitude and phase difference of the stress response fundamental, \( \sigma_3, \sigma_5, \ldots \), are harmonic amplitudes, and \( \delta_3, \delta_5, \ldots \), are the harmonic phase differences. The nonlinear stress wave of Figure 4c can thus be resolved by Fourier expansion into a fundamental wave and its harmonics as in Figure 4e; and since the fundamental wave obtained is a sine wave of the same frequency as the strain wave, the phase difference \( \delta_1 \) is readily found by experiment. The question is whether the approximation made in using the fundamental is within allowable bounds.

Somewhat more detailed information is given in Figure 5. The various parameters shown in Figure 5 are defined by the Equations (5) to (8):

\[
|G^*| = \frac{s_{\text{peak}}}{g_{\text{peak}}} \tag{5}
\]

\[
G''_1 = \left( \frac{s_1}{\gamma_{\text{large}}} \right) \cos \delta_1 \tag{6}
\]

\[
G''_1 = \left( \frac{s_1}{\gamma_{\text{large}}} \right) \sin \delta_1 \tag{7}
\]

Nonlinearity = \( \sqrt{\sum s_i^2 / s_1^2} \) \( \tag{8} \)

The filled circles are the absolute values of dynamic modulus of elasticity \( |G^*| \), \( \delta \) and \( \Delta \) are the storage modulus \( G'_1 \) and loss modulus \( G''_1 \) found from the fundamental, and the bar graph shows the degree of nonlinearity. Especially problematic is \( G''_1 \) (apparent \( G'' \)). Most papers treating storage modulus on the basis of the Payne effect focus on the peak in \( G''_1 \); but as will be clear from Figure 5, \( G''_1 \) falls away beyond the peak once the harmonics start contributing to spectral density. Hence, it is unclear how much physical significance can be accorded to the peak value of \( G''_1 \) and the strain amplitude corresponding to the peak. Furthermore, as strain dependence increases, a distinct difference emerges between \( |G^*| \) and \( G'_1 \). Use of the fundamental wave from Fourier expansion of the nonlinear response wave corresponds to approximation of the Lissajous figure shown as a solid line in Figure 4f by the dotted eclipse, though this does not in any way make the approximation acceptable. It is possible to take the view that, since \( |G^*| \) and \( G'_1 \) are generally in agreement in the range \( \gamma_{\text{large}} \leq 0.2 \) or thereabouts, treatment in terms of \( G''_1 \) is permissible. Although this appears to be a problem for the investigator rather than a question of merit, it does

![Figure 4](image-url)  
**Figure 4.** (a) Strain wave and stress wave in very small oscillation; (b) Lissajous figure; (c) Sinusoidal strain wave and nonlinear stress wave under large amplitude oscillating deformation; (d) Lissajous figure; (e) Fundamental and harmonic waves of the nonlinear stress wave in (c); (f) Lissajous figure under large amplitude oscillating deformation (solid line) and approximation based on the fundamental wave (broken line)

![Figure 5](image-url)  
**Figure 5.** Strain amplitude dependence of absolute dynamic modulus (○) and apparent dynamic moduli (storage modulus (●) and loss modulus (□)) found from sinusoidal strain wave and fundamental stress wave. The right hand axis corresponds to the contribution of harmonic components. The Lissajous figures for different strains are shown at the top
are freely made once the sample is set up and the button pushed; the results are calculated by the computer and displayed graphically on-screen. The calculation process gone through is not displayed, nor is it explained in the manual. There is no mention of approximation by the fundamental wave found by Fourier analysis. Some rheometers do encourage attention to the handling of measurements obtained under large amplitude oscillation by displaying the degree of nonlinearity in Equation (8), but beyond that no explanation is given. As there is no methodological error, the nonlinearity is reproducible and the graphs look neat and tidy. Even when submitted manuscripts make direct use of the results displayed in large amplitude oscillation measurements, they never point out the fallacy. It seems no-one can sustain real doubt in such a situation. Is it too much for a rheologist to hope that tomorrow’s rheometers will display raw data and make the whole of the data processing transparent? By some method, it must be checked that data from nonlinear rheology measurements are sound enough to withstand scrutiny.

NONLINEAR VISCOELASTICITY OF FILLED RUBBER IN RELATION TO CHANGES IN NETWORK STRUCTURE

Filling with filler and vulcanisation are essential in producing rubber materials. When a crosslinked network coexists with a filler network, compression/deformation recovery can be observed just the filler network [10]. However, an uncured system is more suitable for exploring filled rubber viscoelasticity while looking at the actual filler network. While rubber is an electrical insulator, carbon black (CB) filler is electroconductive; the electrical resistance should thus decrease if a CB filler network is formed and the electrical resistance should rise under large deformation if the filler network is then disrupted. It would hence be useful to make simultaneous observations of mechanical behaviour in large shear deformation and changes in resistance [11].

Figure 6 depicts the dependence on CB filler content of volume resistivity in the undeformed state and the linear dynamic modulus of elasticity. At low filler content the resistance is high and modulus low, but when the filler content is increased, percolation behaviour is apparent in the resistance, with a sharp rise in modulus at high concentrations, above the percolation threshold. Figure 7 compares the results of measurements in an unfilled sample and a 20 phr sample. The unfilled rubber has only weak nonlinearity of modulus and resistance is unaffected by increase in strain. Since no CB filler is present, this result would be expected. When the rubber is filled with CB at 20 phr the modulus shows some strain dependence, but the resistance stays the same whatever the strain. This is because no CB filler network is formed at this concentration. However, the behaviour changes completely above the percolation threshold (Figure 8). The 35 phr sample shows linear behaviour up to a shear strain of 0.01, and the resistance under linear strain remains the same as the pre-deformation value indicated by the broken line during deformation. However, resistance increases greatly at high strain, where strain dependence appears in the relaxation modulus. The linear/nonlinear transitions in electrical resistance and viscoelasticity are entirely consistent. As the CB concentration is increased further, the strain...
dependence of relaxation modulus increases, but the strain dependence of resistance decreases. Although discrepancies of this kind exist, the characteristic feature of linear/nonlinear transition is unaffected. Hence, a CB filler network is undoubtedly involved in the strong nonlinearity of viscoelasticity in CB filled rubber. Note, though, that nonlinearity in viscoelasticity is evident below the threshold in the concentration range where a CB filler network has presumably still to form. Figure 9 shows a schematic model that incorporates these features.

The chief components of the model system are the polymer and the filler. Their interactions may be broadly divided into polymer-polymer, polymer-filler, and filler-filler interactions, and the factors operative in nonlinear viscoelasticity would hence be the response of the chain entanglement network (CeN), the bridged filler network (BFN) involving molecular chains whose ends are constrained by filler gel, and the CB contact filler network (CFN). The manifestation of filler reinforcement effect and marked nonlinear viscoelasticity may be attributed to formation and disruption of the CFN, and the nonlinearity of viscoelasticity at CB 20 phr would be expected from BFN disruption. The model can be further refined on this basis. Thus, all three networks, CeN, BFN and CFN, should contribute to the overall stress; denoting their respective contributions \( \sigma_{\text{CeN}} \), \( \sigma_{\text{BFN}} \) and \( \sigma_{\text{CFN}} \), we may write the total stress \( \sigma \) as the sum of the three contributions, since stress is additive:

\[
\sigma = \sigma_{\text{CeN}} + \sigma_{\text{BFN}} + \sigma_{\text{CFN}} \tag{9}
\]

The first term \( \sigma_{\text{CeN}} \) would depend on the number of entanglements per unit volume, while \( \sigma_{\text{BFN}} \) would depend on the number of entanglements constrained at the filler aggregate/polymer interface per unit volume. Hence, it will be supposed that the relaxation modulus can be written:

\[
G(y; t; \phi) = (1 - \phi)G_{\text{CeN}}(y; t; \phi = 0) + \phi G_{\text{BFN}}(y; t; \phi = 1) + G_{\text{CFN}}(y; t; \phi) \tag{10}
\]

where \( \phi \) is the CB volume fraction. The relaxation modulus of an unfilled CB sample should depend solely on the first term of Equation (10) while the relaxation modulus of a CB 20 PHR sample should depend on the first and second terms, and the relaxation modulus of samples of higher CB concentration should depend on all three terms. This would mean that the contributions of the three networks can be separately evaluated by successively fitting Equation (10) to the relaxation modulus data. The results are shown in Figure 10. The CFN term makes no
contribution in the 20 phr sample (Figure 10f) and the contributions of the CeN and BFN terms are about equal. In the 35 phr sample (Figure 10e) the BFN term makes a greater contribution than the other terms. However, once percolation is sufficiently advanced, the CFN term in modulus becomes dominant. The contribution of CFN grows rapidly with increase in CB concentration. The contribution of BFN can still be distinguished at high CB concentrations, though the relative contribution is then reduced. The contribution of CeN is very small at high CB concentration, though never completely excluded. Taking Figure 10 as a whole, we can say that the important element at low CB concentration is the bridged filler network while at high CB concentration the contact filler network becomes important. The contact filler network appears to be far weaker than the bridged filler network. Hence, the strong strain dependence of viscoelasticity at high CB concentration is attributable to the dominance of the contact filler network. Also characteristic is the increasing dominance of the bridged filler network in the high strain region. A key factor in moulding processes for filled systems would thus be the bridged filler network.

Figure 11 shows the relaxation modulus, volume resistivity and differential storage modulus at a point 5 seconds after stepwise imposition of strain, together with the strain and CB concentration dependence of the differential storage modulus [13] as predicted from relaxation modulus with the BKZ constitutive equation [12]. The observed volume resistivity and differential storage modulus in the nonlinear region clearly peak at a medium CB concentration. It follows that the extremely strong nonlinearity of filled but uncured rubber is due to disruption of the contact filler network, which is a weak network, but that at high CB concentration there is a self-healing effect and fairly rapid network recovery. The prompt self-healing nature of the contact filler network appears to be a key factor in making filled rubber practicable.

RELAXATION TIME OF CB FILLER CONTACT NETWORK STRUCTURE

Lastly, let us consider the dynamics of the weak contact filler network. Both the vulcanisation network and bridged filler network are strong networks. Hence, since the strong networks support the stress, the CB contact network is masked in measurements under deformation conditions. Some other means of measurement must be developed to evaluate the CB contact network; that is, while the filler network must in practice rupture to be observed, the strong networks must be apparently eliminated from the observations. Since we are observing a mechanical response, a state must be reached in which the network chains are unstretched, i.e. the stress is relaxed, meaning that reversible deformation must be used; however, completely reversible stretching deformation is difficult to accomplish. The large compression/recovery deformation procedure shown in Figure 12 was therefore devised [10]. Although both the chemical network and filler network are affected when large compression is applied, the chemical network should revert to its
original state once the deformation is restored. However, since the filler network is weak, some disruption may be anticipated. Disruption of the network should then be reflected in change in dynamic modulus. This is the conceptual basis of the compression/deformation recovery ("reversing double step deformation") method. Figure 13 shows the course of structural recovery in the CB filler network thus observed; and Figure 14 shows the CB aggregate size dependence of relaxation time estimated by the same method [10]. Clearly, the filler contact network is a recoverable network whose recovery relies on diffusion of the CB aggregates.

The relaxation time of CB aggregates merits further consideration [14]. The relaxation time $\tau$, signifies the time required for the centre of gravity of a body in motion to diffuse through space of the same order of size as itself, and can thus be written as in Equation (11):

$$\tau \sim R_{\text{aggregate}}^2 / D_{\text{aggregate}}$$  \hspace{1cm} (11)

where $R_{\text{aggregate}}$ and $D_{\text{aggregate}}$ are respectively the equivalent sphere diameter and diffusion constant of the CB aggregate. The diffusion constant $D_{\text{aggregate}}$ may be written as in Equation (12):

$$D_{\text{aggregate}} \sim kT / \zeta_{\text{aggregate}}$$  \hspace{1cm} (12)

where $k$, $T$ and $\zeta_{\text{aggregate}}$ are respectively the Boltzmann constant, absolute temperature and the coefficient of friction of the CB aggregate particles. From the Stokes-Einstein law, $\zeta_{\text{aggregate}}$ may be expressed as Equation (13):

$$\zeta_{\text{aggregate}} \sim 6 \pi \eta_{\text{local}} R_{\text{aggregate}}$$  \hspace{1cm} (13)

where $\eta_{\text{local}}$ is the local viscosity of the matrix polymer. Hence, $\tau$ is given by Equation (14):

$$\tau \sim 6 \pi \eta_{\text{local}} R_{\text{aggregate}}$$  \hspace{1cm} (14)

$\eta_{\text{local}}$ and $R_{\text{aggregate}}$ would not be expected to depend on either CB concentration or strain. The relaxation time characteristic of the CB filler contact network should therefore show the following characteristics:

(a) $\tau$ is independent of CB loading,

(b) $\tau$ is independent of the strain applied to the CB filled rubber, and

(c) $\tau$ is directly proportional to $1/T$.

As shown in Figure 15, these predictions are in agreement with the experimental results.

Applying a similar analysis to time-temperature equivalence factors, we would expect the time shift factor to depend solely on the matrix polymer, not on the nature or loading of the filler, whereas the modulus shift factor would depend on the filler network structure, as has been demonstrated experimentally [15].
CONCLUSIONS

The rheology of rubber is intimately associated with a number of different structures, and the changes in internal structure of the material under large stimulus are sensitively reflected in mechanical nonlinearity. That is what makes the rheology so significant. However, simple phenomenological treatment of the relation between stimulus and response is not enough; the change in internal structure and rheological response to large stimulus must be observed at the same time. In observing the structural change in carbon black filled systems, it is highly effective to supplement measurements of large deformation response with concurrent measurements of perturbation/superimposed stimulus response and change in electrical resistance. More recently, the CB contact filler network structure under deformation has also been observed by 3D-TEM [16]. It is hoped that further progress will be made in the rheological analysis of rubber materials based on observation of structural change.

REFERENCES


Figure 15. Temperature dependence of relaxation time of filled SBR at different CB concentrations and the strain found by the superimposed small oscillatory compression/deformation recovery method.