Comparison of Dynamic Shear Properties of Styrene–Butadiene Vulcanizates Filled with Carbon Black or Polymeric Fillers

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ABSTRACT: The dynamic shear behavior of SBR 1500 vulcanizates filled with polymeric fillers of 24.6, 40.2, and 74.7 nm diameter and various filler loading up to 100 phr (parts per 100 parts of rubber), and its dependence of strain amplitude up to 14%, have been investigated. The results are compared with carbon-black-filled vulcanizates. The reinforcement ability of polymeric fillers is comparable to that of carbon black, depending on filler particle diameter. As expected, the smaller particles have a higher reinforcement effect than larger particles. The Payne effect, that is, the decrease of storage shear modulus G' with increasing strain amplitude and the appearance of a loss modulus G'' maximum at strains of a few percent, has also been observed in vulcanizates with polymeric fillers. The loss modulus maximum of vulcanizates filled with polymeric fillers is at higher strain amplitudes and is less pronounced than for carbon-black-filled vulcanizates. The results are discussed shortly in terms of recent models based on the idea of filler networking within the rubbery matrix. The experimental G' data are adjusted with the deagglomeration–reagglomeration Kraus model (1984). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 495–503, 1999

Key words: filled rubber; carbon black; polymeric fillers; Payne effect; filler net-working

INTRODUCTION

Elastomers are used in a wide range of applications, particularly in automotive tires, under several conditions of temperature, frequency, and deformation. Different types of fillers, especially carbon black and silica, are added to adjust performance properties of tires like wet skid resistance, rolling resistance, and wear resistance. These active fillers affect the properties of vulcanizates more than the mere addition of hard dispersed particles to a soft polymer matrix (hydrodynamic effect).

Carbon black networking is connected with dissipation mechanisms. But up to now, there is no full understanding for the physical processes behind, especially for the description of rolling resistance. Its reduction is an important aim of the current tire development, which cannot be solved only by the use of carbon black fillers. For this aim, the partial substitution by polymeric fillers is expected to be suitable.

The reinforcement ability (for review, see Donnet et al.¹ and Medalia²) of carbon black is related to the complex structure of this filler. The spher-

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Figure 1 Modulus contributions as a function of strain (schematically; also see Donnet et al.¹ p. 313).

ical primary carbon black particles, ranging from 18 to 70 nm, have a rough and energetically heterogeneous surface. Therefore, they form mechanically stable aggregates in the 100-nm range that will not be disturbed during processing, which, in turn, form agglomerates of less stability.

Carbon-black-filled rubbers show a typical nonlinear viscoelastic behavior. At strains of about 1%, a significant decrease of storage modulus occurs from the zero-strain value G'_0 to a highamplitude plateau value G'_{∞} connected with the appearance of a loss modulus G'' maximum. This effect was described by Payne in the 1960s.^{3,4} He interpreted this behavior as the result of breakage and reforming of physical bonds between the filler aggregates. These bonds were assumed to build filler agglomerates of different size and, above a certain threshold, an elastic filler network within the rubber matrix.

A general schematic illustration of reinforcement in filled vulcanizates is given in Figure 1 (also see Donnet et al.,¹ p. 313). The modulus is composed of the following parts, which do not depend on strain: the pure rubber network, the hydrodynamic effect, specific filler-matrix interactions, and in addition, a strain-dependent part caused by the filler network. Based on an agglomeration-deagglomeration mechanism between the aggregates within the filler network (this is the idea of Payne^{3,4}), Kraus⁵ proposed a phenomenological model for the Payne effect of carbonblack-filled rubbers. Very recently, some more molecular models were published that support the idea of filler networking.⁶⁻⁸

This article deals with the reinforcing ability of solid spherical polymeric filler particles with diameters comparable to the size of carbon black primary particles. The Payne effect of vulcanizates filled with these polymeric fillers is compared with that of carbon-black-filled ones.

PROPERTIES OF CARBON BLACK AND POLYMERIC FILLERS

As mentioned above, the reinforcing ability of carbon black is related to its complex structure. Carbon black is composed of primary particles, ranging from 18 to 70 nm, inseparably fused together to form stable aggregates, the size of which varies from 50 to some hundred nanometers. These aggregates are known to form agglomerates with low mechanical stability.

Parameters like the specific surface area and surface structure are used to characterize carbon blacks. Adsorption methods based on nitrogen, cetyltrimethyl ammonium bromide (CTAB), or iodine are usually used to determine the specific surface area (also see Donnet et al.,¹ pp. 116– 120). Such surface area values may differ of each other. Nitrogen surface areas of commonly used reinforcing blacks are of the order of 100 m²/g.

The structure of carbon black and the degree of ramification of agglomerates is caused by the specific arrangement of primary particles within the aggregates determining formation and size of empty spaces. It is generally accepted that carbon black can be considered as a multifractal, as shown in Gerspacher et al.⁹

In contrast, the polymeric fillers investigated in this article consist of solid, highly crosslinked spherical particles with diameters of (24.6 ± 2.4) , (40.2 ± 5) , and (74.7 ± 14) nm. These diameters are comparable to the carbon black primary particle diameter. But contrary to carbon black particles, the polymeric filler particles do not form stable aggregates. Therefore, this filler system is of less complexity than carbon black.

KRAUS MODEL

Kraus⁵ suggested a phenomenological model to describe the strain dependence of carbon-black-

filled rubbers. He assumed that aggregate-aggregate contacts (van der Waals interactions) are continuously broken and reformed under a periodic sinusoidal strain at fixed frequency and temperature, $\gamma = \gamma_a \sin(\omega t)$. Therefore, in filled rubbers above the percolation threshold, the carbon black aggregates form a temporary secondary network within the rubbery polymer network. A deagglomeration rate (breakage rate) R_d is assumed to be proportional to the number of consisting contacts N and to some power m of the amplitude, γ_a^m . The reagglomeration rate R_r is assumed to be proportional to the difference between the number of possible (elastically effective) contacts at zero deformation N_0 and the number of existing contacts N. Furthermore, R_r is assumed to vary as γ_a^{-m} . Then, we have the following.

Deagglomeration rate: $R_d = k_d \gamma_a^m N$,

Reagglomeration rate: $R_r = k_r \gamma_a^{-m} (N_0 - N),$ (1)

where k_d and k_r are the two rate constants.

Deagglomeration and reagglomeration rates are equal at the rate equilibrium, that is, $R_d = R_r$. Then we obtain from eq. (1),

$$N = \frac{N_0}{1 + (\gamma_a/\gamma_0)^{2m}}, \quad \gamma_0 = \left(\frac{\mathbf{k}_r}{\mathbf{k}_d}\right)^{1/2m}, \qquad (2)$$

where γ_0 is a characteristic strain amplitude.

Assuming that the excess modulus of the agglomeration network is proportional to the number of currently existing contacts, one obtains

$$\frac{G' - G'_{\infty}}{G'_0 - G'_{\infty}} = \frac{N}{N_0} = \frac{1}{1 + (\gamma_0 / \gamma_0)^{2m}},$$
(3)

where G'_0 is the storage modulus for zero deformation, and G'_{∞} is the corresponding modulus for large deformations (plateau value at large strains). With $\Delta G' = G'_0 - G'_{\infty}$,

$$G'(\gamma_a) = G'_{\infty} + \frac{\Delta G'}{1 + (\gamma_a/\gamma_0)^{2m}}.$$
 (4)

This phenomenological formula for the strain dependence has been successfully applied to carbon-black-filled vulcanizates.¹⁰ Because no special restrictions concerning the filler properties were used, we also may try to apply this model to describe the effects of polymeric fillers.

The four parameters of eq. (4) have the following physical meanings: G'_{∞} is the storage modulus of the pure rubber matrix increased by the hydrodynamic filler effect and specific filler-matrix interactions (see Fig. 1), $\Delta G'$ is the excess storage modulus of the temporary secondary filler network (which will be destroyed with increasing strain amplitude), and γ_0 is a characteristic strain amplitude, determined mainly from the ratio of the rate constants. The loss modulus maximum is at γ_0 . The *m* exponent has been introduced by Kraus as an empirical parameter. This exponent can be related to the connectivity of the filler network and can be determined from the fractal dimension of the percolation clusters.⁸ The study of different carbon-black-filled rubber compounds yields an exponent m of about 0.6.¹¹ Obviously, within a certain range, the amount of *m* is nearly independent of temperature, frequency, and carbon black loading. However, m depends on the embedding polymer matrix.^{11,12}

Formulas for G'' and tan δ can be obtained in a similar manner, for example,

$$G''(\gamma_a) = \frac{\Delta G'(\gamma_a/\gamma_0)^m}{1 + (\gamma_a/\gamma_0)^{2m}}.$$
(5)

The fit of G'' strain sweeps by eq. (5) is not as good as for G' sweeps, and the parameters of the two fits are usually different.¹⁰ Therefore, this discrepancy indicates some incompleteness of the Kraus model.

EXPERIMENTAL

Materials

The matrix materials are emulsion-polymerized styrene-butadiene rubbers containing 23 wt % styrene groups (SBR 1500). The compound recipe is given in Table I. The vulcanizates were filled with 25, 50, 75, and 100 phr (parts per 100 parts of rubber) polymeric fillers with diameters of 24.6, 40.2, and 74.7 nm (also see Table II) and, in addition, carbon-black-filled compounds with the same phr loadings were used as reference. The loadings correspond to volume fractions ranging from $\varphi = 0.172$ to 0.453 for polymeric fillers and from $\varphi = 0.103$ to 0.315 for carbon black, respectively (also see Table III). The polymeric fillers consist of highly crosslinked high-cis polybuta-

| SBR 1500 Vulcanizate Ingredients | ulcanizate Parts Per 100 Parts of Rubber ients (phr) | |
|-------------------------------------|--|--|
| E-SBR 1500 | 100 | |
| Filler (all types) ^a | 0, 25, 50, 75, or 100 | |
| Aromatic oil | 8 | |
| Antisunchecking agent | 1 | |
| Phenolic resin | 1 | |
| Stearic acid | 2 | |
| Zinc oxide | 3 | |
| IPPD ^b | 1 | |
| DTPD ^c | 1 | |
| Sulfur | 1.8 | |
| CBS^d | 1.5 | |
| DPG ^e | 0.3 | |

Table ICompound Recipe for the SBR 1500Vulcanizates

^a Carbon black, N 339; polymeric filler, see text.

 $^{\rm b}$ IPPD: $N\mbox{-}{\rm isopropyl-}N'\mbox{-}{\rm phenyl-}p\mbox{-}{\rm phenylene}$ diamine.

^c DTPD: *N*,*N*'-ditolyl-*p*-phenylene diamine.

^d CBS: benzothiazyl-2-cyclohexyl sulphenamide.

^e DPG: *N*,*N*'-diphenyl guanidine.

diene. The samples, supplied from Deutsches Institut für Kautschuktechnologie (DIK), were prepared by mixing the compound ingredients on a two-roll mill, molded, and cured at 150°C for a specified time to ensure optimum cure. The crosslinking of the matrix material with 1.8-phr sulfur leads to a molecular weight between two crosslinks of about 5000 g/mol estimated by ¹H nuclear magnetic resonance (¹H-NMR) Hahn spin echo technique.¹³

The diameter of polymeric filler particles has been estimated by ultracentrifugation.¹⁴ The particle–size distribution is narrow (see Table II). The glass temperature of the polymeric filler could not be determined by differential scanning calorimetry (DSC) because the heat capacity step

Table II Filler Characteristics

| Filler | Diameter (nm) | Diameter Dispersion (nm) | Specific Surface (m ² /g) |
|---|---|--------------------------------|---|
| Polymeric, 24.6 Polymeric, 40.2 | $\begin{array}{c} 24.6 \\ 40.2 \end{array}$ | 2.45 | 246^{a} 149^{a} |
| Polymeric, 74.7 Carbon black, N 339 | 74.7 26 | 14 | $\begin{array}{c} 80^{\mathrm{a}} \\ 94^{\mathrm{b}} \end{array}$ |

^a Calculated from geometry assuming $\rho = 1$ g/cm³.

 $^{\rm b}$ N $_2$ adsorption

Table IIIFiller Volume Fraction

| Loading (phr) | Filler Volume Fraction ^a | | |
|------------------|-------------------------------------|------------------|--|
| | Carbon Black | Polymeric Filler | |
| 25 | 0.103 | 0.172 | |
| 50 | 0.187 | 0.293 | |
| 75 | 0.257 | 0.383 | |
| 100 | 0.315 | 0.453 | |
| | | | |

^a Calculated from the recipe given in Table I with density of N 339 black, $\rho = 1.8 \text{ g/cm}^3$. Density of further incredients (20.6 phr) is assumed to be about 1 g/cm³.

height Δc_p decreases, and the glass temperature interval increases with increasing crosslink density. Dynamic shear experiments show an extremely broad maximum of the loss factor tan δ at 1 Hz at a temperature of about 100°C. Thus, in this study, the polymeric filler can be assumed to be in the glassy state at temperatures up to 50°C, which means that the fillers can be assumed as hard, undeformable particles. The geometrical surface areas of these particles are 246 m²/g for the 24.6-nm, 149 m²/g for the 40.2-nm, and 80 m²/g for the 74.7-nm diameter particles, respectively.

The specific surface area of the N339 carbon black used is $94 \text{ m}^2/\text{g}$ (N₂ adsorption), the primary particle size is 26 nm. Therefore, surface area and particle diameter of are of the same order.

Methods

A Rheometric Scientific RDA II mechanical analyzer was used for shear measurements. Frequency sweeps were performed in the range from 0.1 to 100 rad/s (10 points per decade) and in the temperature range from -60 to -10° C (5-K steps) at 0.2% strain. The specimen stripes have a length of about 20 mm, a width of about 10 mm, and a thickness of about 2 mm. The frequency sweeps were mastered at a reference temperature of -30° C with the RHIOS 4.22 software.

The strain dependence of the dynamic modulus G^* was determined by increasing the strain amplitude from 0.01 to 14% (10 points per decade) at a constant temperature of 20°C and a frequency of 1 Hz. The specimen length for the strain sweeps was only 10 mm to achieve larger strains. This small specimen length leads to a certain systematic error of the experimental data of the strain sweeps. But the results remain comparable because the same stripe length was used for all



Figure 2 Master curves of SBR 1500 vulcanizates: unfilled, filled with carbon black N 339, or polymeric fillers with a particle diameter of 40.2 nm (reference temperature, -30° C; strain amplitude, 0.2%).

samples. The effect of the systematic error on the model parameters was estimated to be small.

RESULTS AND DISCUSSION

Frequency Sweeps

The polymeric filler influences the storage modulus G', loss modulus G'', and loss factor tan δ in the rubbery zone similarly to carbon black (Fig. 2, master curves of unfilled, carbon-black-filled vulcanizates, and vulcanizates filled with the polymeric filler of diameter 40.2 nm of different loading at a reference temperature of -30° C). This means that the reinforcing ability of the polymeric filler is of order of carbon black. At 25, 50, and 75 phr loadings, the plateau modulus of the vulcanizates filled with polymeric filler is larger than that for carbon black fillers at comparable phr loadings. This is caused by the different filler densities, as follows: the volumetric amount of polymeric filler is higher than the carbon black amount at the same phr loading. For 100-phr loading, however, the carbon-black-filled vulcanizate has a larger plateau modulus.

The difference of the glass modulus and plateau modulus logarithms is always smaller for vulcanizates filled with polymeric fillers (\emptyset 40.2 nm) than for carbon black fillers at the same phr loading.

The storage modulus in the glassy zone of vulcanizates with polymeric fillers is practically not influenced by the filler amount because the glass shear moduli of the polymeric filler and of the polymer matrix are comparable. The carbonblack-filled compounds show a slightly increase of the glass modulus caused by the higher carbon black shear modulus.

In all cases, the location of the loss modulus maximum of the vulcanizates is not affected by the filler type, neither by carbon black nor polymeric fillers. This is in good agreement with DSC measurements: The compound glass temperature does not depend on filler type and loading. (DSC glass transition temperatures and G'' maximum frequencies are listed in Table IV).

The loss factor maximum tan δ_{max} decreases, and its position is shifted to higher frequencies with increasing filler content. Since this is the transition zone of the rubber matrix, that is, the transition from the glassy to the rubbery zone, this behavior indicates that the reinforcing fillers affect molecular motions with mode lengths of order of several nanometers.¹⁵

Strain Sweeps

As shown in Figure 3, the strain dependences of vulcanizates for different phr loadings with polymeric filler or carbon black filler behave qualitatively similar. In both cases, we observe the Payne effect, that is, a decrease of the storage modulus with increasing strain amplitude, connected with a maximum of the loss modulus. For vulcanizates with polymeric fillers, the decrease of storage modulus and the maxima of loss modulus and loss factor occur at higher strains and

| Sample | | | |
|---------------------------|-------------------------|---------------------|---|
| Particle Diameter (nm) | Filler Content (phr) | T_g (°C) (DSC) | $\begin{array}{c} \log \ \omega(G''_{\max}) \ (\mathrm{rad/s}) \ \mathrm{at} \ -30^{\circ}\mathrm{C} \\ (\mathrm{Shear}) \end{array}$ |
| No filler | Unfilled | -49.2 | 4.31 |
| Carbon black N 339 | 25 | -47.9 | 4.25 |
| Carbon black N 339 | 50 | -48.8 | 4.07 |
| Carbon black N 339 | 75 | -48.9 | 4.03 |
| Carbon black N 339 | 100 | -48.4 | 4.08 |
| Polymeric, 24.6 | 25 | -48.5 | 4.30 |
| Polymeric, 24.6 | 50 | -48.2 | 4.32 |
| Polymeric, 24.6 | 75 | -49.5 | 4.44 |
| Polymeric, 24.6 | 100 | -49.4 | 4.46 |
| Polymeric, 40.2 | 25 | -48.7 | 4.35 |
| Polymeric, 40.2 | 50 | -49.4 | 4.11 |
| Polymeric, 40.2 | 75 | -49.3 | 4.33 |
| Polymeric, 40.2 | 100 | -49.2 | 4.35 |
| Polymeric, 74.7 | 25 | -48.9 | 4.28 |
| Polymeric, 74.7 | 50 | -49.3 | 4.04 |
| Polymeric, 74.7 | 75 | -48.7 | 4.16 |
| Polymeric, 74.7 | 100 | -49.0 | 4.17 |

Table IV DSC Glass Temperatures T_g and Frequency of the Maximum Shear Loss Log $\omega(G''_{\text{max}})$ at $T = -30^{\circ}$ C of Filled Vulcanizates

are less pronounced as for carbon-black-filled vulcanizates. An intuitive explanation could be that the filler-matrix contact is softer for the polymeric fillers.

Figures 4 and 5 show the strain sweeps for different filler sizes for identical filler weight (phr) and filler volume fractions, respectively. The storage modulus G' is strongly influenced by the polymeric filler particle size: Smaller particles yield higher moduli. This indicates that the volumetric filler amount is not the only interesting parameter. An intuitive explanation is that shorter particle–particle distances immobilize large network mode lengths. This implies (via the fluctuation dissipation theorem¹⁵) higher shear moduli of the matrix.

The particle–particle distance or a certain rubber shell around the filler may play a dominant role on vulcanizate properties. This is in accordance with the assumption of the network junction model $(njm)^{16}$ that the filler–filler attractive force and interaggregate distance are the controlling factors for the dynamic hysteresis having a maximum at medium strain. In the njm model, the contacts between polymeric filler particles are established by a layer of the matrix polymer that is called junction rubber. If the energy loss takes place near the peripherals of the rubber–filler interface, the dissipated energy for a cyclic displacement can be due to the following two reasons: the actual interfacial slippage between rubber matrix and filler particles and/or the rubber internal friction near these regions. A reduction of tan δ as a function of strain would then be obtained by improved microdispersion of the filler particles or loosening up the filler network.

The storage modulus G' as function of the strain amplitude γ_a of the strain sweeps were analyzed with the Kraus model [eq. (4)]. Figure 6 shows an example of fit results and the deviation plot. The deviations for polymeric fillers are of order of 1%. The Kraus model parameters have an uncertainty of about 2% for $\Delta G'$ and G'_{∞} and 15% for m, γ_0 because the region of large strain modulus could not been reached in our device and because the parameters γ_0 and m are interdependent.

The Kraus fit parameters, G'_{∞} , $\Delta G'$, γ_0 , and m, of all filled vulcanizates are shown in Figure 7, including the parameters for carbon black fillers. Both the modulus at large strain G'_{∞} and the modulus difference between zero and large strains $\Delta G'$ increase strongly with increasing filler content and decreasing particle size. Both modulus values for carbon black fillers are higher at a comparable volumetric filler content φ .

The characteristic strain amplitude γ_0 of the carbon-black-filled vulcanizates is significantly smaller than for polymeric fillers.



Figure 3 Strain sweeps of SBR 1500 vulcanizates filled either with carbon black N 339 or polymeric fillers with a particle diameter of 40.2 nm (temperature, 20°C; frequency, 1 Hz).

The Kraus parameter m tends to increase with filler content and decreasing filler particle size. A value of m = 0.6 was estimated in a recent work for carbon-black-filled vulcanizates.¹¹

A theoretical model has recently been developed that establishes a correlation between the strain dependence of the elastic deformation of filled rubbers and the structure of the filler clusters.⁸ In this model, the exponent m is solely related to the connectivity of the filler clusters, independent of the filler type and the physical nature of the couplings between the filler particles (for example, van der Waals aggregate-aggregate bonds in the case of carbon black or junction rubber couples between polymeric fillers, as mentioned above). It was found that m(C) = -(C - 2)/(C - 1), where *C* is the connectivity exponent in the scaling relation

$$N = (\xi/b)^C. \tag{6}$$

Here, N is the number of elastically active filler particles of size b in a typical cluster of size ξ (correlation length). The term "elastically active" means that in irregular fractal structures, many



Figure 4 Strain sweeps of SBR 1500 vulcanizates filled with 75 phr carbon black N 339 or 75-phr polymeric fillers with particle sizes of 24.6, 40.2, and 74.7 nm (temperature, 20°C; frequency, 1 Hz).



Figure 5 Strain sweeps of SBR 1500 vulcanizates of identical filler volume fraction ($\varphi = 0.3$) filled with 100-phr carbon black N 339 or 50-phr polymeric fillers with particle sizes of 24.6, 40.2, and 74.7 nm, respectively (temperature, 20°C; frequency, 1 Hz).

structural elements (e.g., dangling and nonconnected parts) do not take part in the transmission of stress. From the value of $m \approx 0.6$, a connectivity exponent of $C \approx 1.625$ is calculated. In an ideal percolation cluster, this exponent is to be identified with the fractal dimension of the cluster backbone, $C \approx 1.7$.¹⁷ Deviations are expected if the aggregation process for filler clusters is in another universality class of growth processes, as assumed for the m(C) formula used above. This is studied by Klüppel and Heinrich,¹⁸ where, additionally, the effects of dispersion during mixing are investigated.

The fitting to the Kraus model for G' and the theoretical finding of an interrelation between the shape exponent m and cluster connectivity⁸ leads to the conclusion that the polymeric fillers are not homogeneously distributed within the rubber matrix. Instead, the filler particles obviously form larger clusters that show self-similar structures between certain cut-off length scales. The clusters break with increasing strain amplitude.

Finally, we note that the quality of curve fits for the storage and loss modulus is the same as using a Langmuir theory of adsorption of matrix chains on the surface of the filler particles to explain the Payne effect in filled rubbers.¹⁹ But, the adsorption model assumes different constant shape exponents m = 0.5 for G' and m = 1 for G''[eqs. (12) and (16) in Maier and Göritz¹⁹]. A more detailed comparison and discussion of the physical models for the explanation of the Payne effect will be given in Huber et al.²⁰

CONCLUSIONS

This article demonstrates the existence of the Payne effect in rubbers filled with polymeric fillers.



Figure 6 Kraus model fit of storage modulus of vulcanizates with polymeric filler (\emptyset 24.6 nm) and deviation plots (temperature, 20°C; frequency, 1 Hz).



Figure 7 Kraus model eq. (4) fit parameters from the storage modulus G' of strain sweeps of filled SBR 1500 vulcanizates (temperature, 20°C; frequency, 1 Hz).

Polymeric fillers of the size of about several ten nanometers have a reinforcing effect on complex modulus of rubbers comparable to carbon black fillers. The moduli in the region between the main transition and the network plateau are strongly influenced by the polymeric filler: Decreasing particle diameter enlarges both storage modulus and loss modulus.

The strain dependence of the storage modulus for the vulcanizates with polymeric fillers can be fitted well to the semiempirical deagglomeration—reagglomeration Kraus model. The modulus for large strains G'_{∞} and the modulus difference be-

tween zero and large strains $\Delta G'$ increase with increasing volumetric filler content and decreasing filler diameter. The characteristic strain amplitude γ_0 is higher than that of carbon-blackfilled compounds.

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