

CRP-213-292

THE ROLE OF FILLER NETWORKING IN DYNAMIC PROPERTIES OF FILLED RUBBER

Meng-Jiao Wang

Paper presented at a meeting of the Rubber Division, American Chemical Society.
Indianapolis, Indiana, May 5-8, 1998

The Role of Filler Networking in Dynamic Properties of Filled Rubber

*by Meng-Jiao Wang**

*Cabot Corporation, Billerica Technical Center
15 7 Concord Road, Billerica, Massachusetts 01821-7001*

Presented at a meeting of the
Rubber Division, American Chemical Society
Indianapolis, Indiana
May 5-8, 1998

* Speaker

ABSTRACT

Fillers when added to polymer systems are known to cause a considerable change in dynamic properties. For a given polymer and cure system, this paper will discuss the impact of the filler network, both its strength and architecture, on the dynamic modulus and hysteresis during dynamic strain. It was found that the filler network can substantially increase the effective volume of the filler due to rubber trapped in the agglomerates, leading to high elastic modulus. The amount of trapped rubber was estimated according to Van der Poel theory. During cyclic strain, while the stable filler network can reduce the hysteresis of the filled rubber, the breakdown and reformation of the filler network would cause an additional energy dissipation resulting in higher hysteresis.

The Role of Filler Networking in Dynamic Properties of Filled Rubber

INTRODUCTION

One of the consequences of incorporation of filler into a polymer is a considerable change in dynamic properties of the rubber, both modulus and hysteresis. This phenomenon has been investigated in depth especially in relation to rubber products. It has been recognized that for a given polymer and cure system, the filler parameters influence dynamic properties in different ways, i.e., multiple mechanisms may be involved. Among others, filler networking, both its architecture and strength seems to be the main (though not the only) parameter to govern the dynamic behavior of the filled rubber.

It is known that the filler aggregates in the polymer matrix have a tendency to associate to agglomerates, especially at high loading, leading to chain-like filler structures or clusters. These are generally termed secondary structure or, in some cases, filler network, even though the latter is not comparable to the continuous three-dimensional polymer network structure. The existence of the filler network and its impact on rubber properties, viscoelastic behavior in particular, have been reviewed in depth in several articles.¹⁻³ With carbon black, silica and carbon-silica dual phase filler as fillers, this study is an attempt to further demonstrate the role of filler networking on dynamic properties by revealing the effect of loading and characteristics of the fillers on strain and temperature dependence.

EXPERIMENTAL

Materials

The fillers used in this study are a carbon black N234 (VULCAN[®] 7H from Cabot), a precipitated silica (HiSil 233 from PPG), a carbon-silica dual phase filler G (CSDPF), and a CSDPF with 3% TESPT (bis(3-triethoxy- silylpropyl-) tetrasulfane) based on weight of the filler. The analytical properties of these fillers are listed in Table I.

[®] VULCAN is a registered trademark of Cabot Corporation.

A solution SBR (SSBR) with bound styrene of 23.5% and vinyl content of 46% was used for compounding according to the formulation shown in Table II.

Preparation of the Vulcanizates

The compounds were mixed in a Brabender Plasticorder using a two-stage mixing procedure with the last stage for adding curatives. The compounds were then cured to an optimum cure state adjusted to according to t_{90} obtained from Rheometer measurement.

Measurement of Dynamic Properties

The dynamic properties of filled vulcanizates were measured by means of a Rheometric Dynamic Spectrometer II (RDS II, Rheometris, Inc., NJ) in two modes, namely strain sweeps and temperature sweeps. In the case of strain sweeps, double strain amplitudes (DSA) ranging from 0.2 to 120% were applied with frequency of 10 Hz at constant temperatures of 0 and 70°C. The data were taken 5 points per decade and the full curves were recorded. The temperature sweep measurements were carried out at temperatures ranging from -60 to 100°C with intervals of 5°C. The test frequency was fixed at 10 Hz and strain amplitude was set at 5% DSA. This strain amplitude remained constant until the temperature decreased below the peak temperature of the loss tangent ($\tan \delta$) curve. With further decreasing temperature (below -25°C for this particular polymer), the strain amplitude decreased as the materials became very hard.

RESULTS AND DISCUSSION

Strain Amplitude Dependence of Elastic Modulus of Filled Rubber

Shown in Figure 1 is a plot of elastic modulus measured at 70 and 0°C and 10 Hz vs. the logarithm of the double strain amplitude (DSA). The vulcanizates are filled with different loadings of carbon black N234. As can be seen, while the modulus of the unfilled compound does not change significantly upon increasing strain amplitude over the range of DSA tested, it decreases for the filled rubber, showing a typical non-linear behavior. This phenomenon was observed in 1950 by Warring⁴ and later it was studied extensively by Payne after whom the effect is often named.^{2,5} This effect is exponentially increased by increasing filler loading. On the other hand, since the moduli of all vulcanizates at high strain amplitude are in a narrow range, an exponential augmentation of the modulus

at low strain amplitudes with increasing filler concentration is also observed. The decrease in elastic modulus upon increasing strain amplitude was attributed by Payne to “the structure of the carbon black, and may be visualized as filler-filler linkages of physical nature which are broken down by straining”.⁶ This structure was further clarified by Medalia as that “interaggregate association by physical forces, not the “structure” or aggregate bulkiness” as generally termed in the rubber industry.³ This suggests that the Payne effect is mainly, if not only, related to the filler network formed in the polymer matrix. It is understandable that the rubber *trapped* or *caged* in the filler network or agglomerates would be at least partially “dead”, losing its identity as an elastomer and behaving as filler in terms of stress-strain properties. Therefore, the effective volume of the polymer bearing the stresses imposed upon the sample is reduced by filler networking, resulting in increased modulus which is governed primarily by the filler concentration. The breakdown of the filler network by increasing strain amplitude would release the trapped rubber so that the effective filler volume fraction and hence the modulus would decrease. This mechanism suggests that the Payne effect can serve as a measure of filler networking which originates from filler-filler interaction as well as polymer-filler interaction. This observation can be verified by the changes in effective volume of filler upon filler loading and their strain dependence.

Several authors have suggested relationships between modulus and loading, the most successful approach being the one proposed by Guth-Gold which is based on the hydrodynamic effect and mutual disturbance caused by sphere particles:^{7,8}

$$G'_f = G'_{gum} (1 + 2.5\phi + 14.1\phi^2) \quad (1)$$

where G'_f and G'_{gum} are shear moduli of filled and gum vulcanizates and ϕ is volume fraction of the filler. It has been found that the application of this equation has been limited to low concentrations of a few carbon blacks, such as thermal carbon blacks which are composed of nearly spherical particles. When the asymmetry of the fillers was taken into consideration, Guth⁹ introduced a shape factor modifying Equation 1 to extend its application to non-spherical fillers but still with validity for concentration up to a few percent only.

Based on the occlusion of rubber internal to the filler aggregates being shielded from the strain/stress seen by the bulk rubber, and acting as part of the filler, Medalia^{10,11} substituted ϕ in equation by ϕ_{eff} which has been calculated from DBP absorption.

$$G'_f = G'_{gum} (1 + 2.5 \phi_{eff} + 14.1 \phi_{eff}^2) \quad (2)$$

Since the shielding is not fully effective, he introduced an occlusion effectiveness factor F to fit the experimental data. Alternatively, Wolff and Donnet¹² introduced a shift factor, f , to convert the filler volume fraction to an effective volume fraction, i.e.,

$$G'_f = G'_{gum}(1 + 2.5 f\phi + 14.1 f^2 \phi^2) \quad (3)$$

This factor reflects all effects of filler properties on modulus through effective loading, with the structure being most important. When this concept was applied to the dynamic elastic modulus, especially that measured at low strain amplitude, it was found that the experimental data of most fillers only fit Equation 3 up to certain levels of loading which is defined as the critical loading, ϕ_{crit} . Beyond this concentration deviations occur with the experimental data being higher than the values calculated from the modified equation. This can be seen in Figure 2a in which the ratio of G' of filled rubber to that of gum, G'/G'_{gum} , measured at 70°C and 10 Hz with different strain amplitudes are plotted as a function of effective volume. The effective volume is obtained from fitting Equation 3 by adjusting the shift factor f . In this particular case f is 1.38 which was derived from the data at DSA 2%. Obviously, the modified Guth-Gold equation is only applicable to the two lowest loadings, namely 10 phr and 20 phr. It was also found that the shift factor is about the same for all strain amplitudes until 2% DSA, beyond which it is slightly reduced with increased strain amplitude. This may be explained by the reduction of the shielding effectiveness of rubber occlusion at high strain. On the other hand, ϕ_{crit} is also slightly but definitely increased with increasing strain amplitudes.

Van der Poel¹³ proposed an equation for the ratio of moduli of the composite filled with rigid spheres at high concentration to the medium modulus, G'/G'_{gum} , which is shown in Figure 3. The equation was based on the assumption that the fillers should be completely dispersed with complete wetting of the filler by the medium, and the rigidity of the filler is much higher than that of the medium. The theoretical values shown in Figure 3,

labeled as Van der Poel, are based on the assumption that the ratio of the rigidity of filler to the medium is 100,000. Shown in Figure 3a is also the ratio G'/G'_{gum} of carbon black filled rubber measured at 70°C at DSA 0.8 and plotted as a function of ϕ_{eff} , instead of ϕ . The ϕ_{eff} were obtained from Equation 3 which includes the effect of hydrodynamic, rubber occlusion and immobilized rubber shell on the filler surface as schematically shown in Figure 4a. As can be seen, all experimental data except that at very low loading, lie far above the theoretical line. For the vulcanizate filled with 50 phr carbon black having $\phi = 0.197$ based on filler density and $\phi_{eff} = 0.276$ derived from Equation 3, the measured G'/G'_{gum} is equivalent to that of the vulcanizate having filler volume fraction of 0.462 obtained from Van der Poel theory. This equivalent filler volume is termed as ϕ_{vap} , as schematically represented in Figure 4b. This suggests that the amount of rubber trapped in the filler network is about 94% of the carbon black volume or equivalent to 67% of the effective volume, ϕ_{eff} , of the filler, even though part of the trapped rubber which overlaps with that immobilized on the filler surface and occluded rubber is excluded. This number varies with filler loading and substantially decreased upon reduction of filler loading and increase in strain amplitude, as shown in Table III.

All observations concluded from the results obtained at 70°C are also evident for 0°C (Figures 1b and 2b) but the difference in moduli between low strain and high strain is much greater, due to the temperature dependence of filler-filler and filler-polymer interaction. It should be pointed out that even though at 0°C the gum is in its transition zone so that the modulus is higher than that obtained at 70°C, from the point of view of kinetic theory, the modulus of the gum or the crosslinked polymer matrix should increase with increasing temperature in the rubber state. However, what is really observed is that when the G' of filled rubber is normalized by that of gum, the G'/G'_{gum} rises much more rapidly at lower temperature. The equivalent volume, ϕ_{vap} , of carbon black in the vulcanizate filled with 50 phr filler is now about 0.523 which is 13% higher than that obtained at 70°C. This may suggest that the filler network is more developed or stronger at low temperature.

Comparison of different types of fillers

If the dynamic modulus and its strain and temperature dependence of filled rubber is mainly related to filler network, its formation would be essentially governed by filler types which possess various filler-polymer and filler-filler interactions. Shown in Figure 5 are the strain dependence of G' of vulcanizates filled with 50 phr carbon black, silica, carbon-silica dual phase filler, and TESPT-modified dual phase filler at both 70 and 0°C.

Compared to carbon black, silica gives high modulus at low strain amplitude and large Payne effect at both temperatures. This would be an indication that a more developed and stronger filler network forms in the silica-filled vulcanizates. This observation can be verified by the equivalent filler volume fraction, ϕ_{vdP} , using the shift factor deduced from the modified Guth-Gold equation (Table III). For example, at 50 phr while the real volume fraction of the filler calculated from density and loading is about 0.176 for silica and 0.197 for carbon black, their ϕ_{vdP} is 0.538 and 0.462 respectively at 70°C and DSA of 0.8%.

The highly agglomerated silica is first attributed to its surface characteristics. It has been recognized that silica possesses a low dispersive component of the surface energy while carbon black is high. By contrast, the specific or polar component of the surface energy is much higher for silica than for carbon black.^{14,15} This suggests that in a hydrocarbon polymer, the polymer-silica interaction which is determined by the dispersive component of filler surface energy is lower, and the interaction between silica aggregates is higher.¹⁶

Consequently less compatibility with polymer and strong filler-filler interaction due to high surface polarity and strong hydrogen bonding between silanol groups would lead to a more developed filler network. On the other hand, the higher surface area of silica may also be responsible for the higher agglomeration as at the same loading, the surface area is the primary factor to control the mean distance between aggregates.¹⁷ The higher the surface area, the shorter the interaggregate distance would be. However, at the same loading, this effect will be, to a certain extent, offset by the difference in density between silica and carbon black.

Also shown in Figure 5 are the results for the vulcanizates filled with CSDPF and its TESPT modified counterpart. Although the dual phase filler is between carbon black and

silica from the point of view of chemical composition, what is actually observed here is that the CSDPF gives lower Payne effect than any of these two conventional fillers. This suggests that the filler networking is lower for CSDPF which would be mainly due to its lower interaggregate interaction. This can also be seen from the plot of G'/G'_{gum} vs. ϕ (or ϕ_{eff}) which is related to the volume fraction of the rubber trapped in agglomerates (Figure 3b and Table III).

The lower filler-filler interaction of CSDPF may involve multiple mechanisms, but it is most readily interpreted on the basis of lower interaction between filler surfaces having different surface characteristics, surface energies in particular. Based on surface energies and interaction between two filler aggregates, Wang¹⁸ derived an equation to show that the same categories of surface would preferentially interact with each other. Accordingly, when dual phase aggregates are dispersed in a polymer matrix, the interaction between the silica domains and the carbon phase of the neighboring aggregates should be lower than that between carbon black aggregates as well as lower than that between silica aggregates. In addition, the portion and the probability of the aggregate surface being able to face directly the same category of surface of the neighboring aggregate is substantially reduced by doping silica in carbon phase. Consequently, there would be less hydrogen bonding, the main cause of the high filler-filler interaction between silica aggregates, between silica domains on neighboring aggregates since their average interaggregate distance would be greater. In addition, from the point of view of flocculation kinetics, the higher surface activity of the carbon phase of CSDPF, which leads to higher bound rubber, may contribute to a less developed filler network¹⁸.

The filler networking of CSDPF can be further depressed by surface modification with coupling agent TESPT as shown by the Payne effect and equivalent filler volume. This is primarily due to the reduction of surface energies, both dispersive and polar components. The higher bound rubber content of the MCSDPF vs. its unmodified counterpart (45 vs. 32%) may also be a reason as the flocculation rate of the filler aggregates may be significantly reduced during vulcanization.

Strain Amplitude Dependence of Viscous Modulus of Filled Rubber

The strain dependencies of viscous modulus for vulcanizates having different loading of N234 are shown in Figure 6 for the results obtained at both 70 and 0°C. Over the whole range of strain amplitude used in this study, G'' is substantially increased by addition of carbon black. This effect is also augmented exponentially with filler loading. The increase in G'' with increasing filler loading may be primarily attributed to the hydrodynamic effect as the addition of unstrained particles in the polymer matrix would result in a high viscosity compound. It is also evident that in contrast to G' of filled rubber which decreases monotonously with increasing strain, G'' shows maximum values at a moderate strain amplitude. After passing through a maximum, the G'' decreases rapidly with further increase in strain amplitude. Such behavior of the strain dependence of filled rubber cannot be explained only by the hydrodynamic effect since the G'' values of the gum compound while being lower, do not give a significant strain dependence over a large practical range of strain amplitudes.

Payne believed that the energy loss of the filled rubber, hence the loss modulus, during dynamic strain is substantially controlled by the breakdown and reformation of the aggregate contacts¹⁹ or said filler network. Kraus²⁰ derived an equations for viscous modulus based on breakage rate of interaggregate contacts and the rate of reagglomeration which are, of course, related to the strain amplitudes. The breakdown of the filler network would increase with increasing strain amplitude, and the reformation of this structure would diminish more rapidly than its disruption. Once the strain amplitude is high enough so that the filler network is destroyed to such an extent that it cannot be reconstructed in the time scale of the dynamic strain (frequency),^{1,19} the effect of filler network on the G'' will disappear. Similarly, if the filler network is strong enough and the strain (or stress) is small enough that the filler network is unable to be broken down, the G'' would be determined mainly by the hydrodynamic effect of the filler so that the strain dependence would be eliminated. In this case however, the effective volume fraction of the filler hence the absolute G'' would be higher due to the hydrodynamic effect.

At the same mass loading, compared to carbon black, silica gives higher G'' and lower values were obtained with CSDPF. The TESPT-modification of CSDPF is able to further

reduce the hysteresis of the vulcanizate (Figure 7). This is true at both high and low temperatures. Lower G'' suggests that for CSDPF less filler network would be broken down and reformed during dynamic strain.

Strain Amplitude Dependence of Loss Tangent

By its definition, the loss tangent is a ratio of G'' to G' which is representative of work converted into heat (or the work absorbed by the compound) to that recovered, for a given work input during dynamic strain. Besides the hydrodynamic effect, the influence of filler on G' and G'' involves different mechanisms and different strain dependencies, with both mechanisms influencing $\tan \delta$. While G' is mainly related to filler network which subsists during dynamic strain, G'' is related to the breakdown and reformation of these structures. Consequently, beyond the contribution of polymer matrix, the factors predominantly determining $\tan \delta$ would be the state of filler-related structures, or more precisely, the ratio between the portion capable of being broken-down and reconstituted and those remaining unchanged during dynamic strain²¹. The change in $\tan \delta$ from changing strain amplitude would reflect the ratio of these two processes.

Presented in Figure 8 is the strain dependence of $\tan \delta$ at 70 and 0°C for carbon black-filled vulcanizates with various loadings. Similar to the effect of strain amplitude on G'' of filled rubber, $\tan \delta$ at 70°C is shown to increase with increasing DSA at lower strain amplitude up to a high level after which there is a gradual reduction. Also like the observations of G' and G'' , strain dependence drastically increases with increasing filler concentration, with basically no significant strain dependence being observed for gum rubber. In addition, compared with G'' , the maximum appears at higher DSA.

Since for the unfilled compound there is no strain dependence for either G' or G'' , for the filled compound, the great increase in $\tan \delta$ upon increasing strain amplitude at low DSA reflects an increase in G'' and a decrease in G' , both contributing to higher loss tangent. With further increase in DSA, G' continuously drops as the filler network structure is further disrupted, the G'' passes its maximum and then decreases as the rate of filler reformation drops more rapidly than its disruption. When the rate of decrease of G'' is

more rapid than that of G' , the $\tan \delta$ -DSA curve drops. Consequently, the $\tan \delta$ maximum appears at a higher strain amplitude than that of G'' .

The discussion so far concerns results obtained at relatively high temperature where the main cause of energy dissipation is related to the change of filler network structure during cyclic strain as the polymer is in its rubbery state with very high entropic elasticity and low hysteresis. When dynamic stress is applied to the filled rubber at temperatures which fall in the transition zone of the polymer, the hysteresis of the polymer needs to be taken into consideration.

As clearly shown in Figure 8b, at 0°C , a temperature in the transition zone of the polymer used, the picture is quite different from that observed at 70°C . Over a certain range of strain amplitudes, $\tan \delta$ decreases with increasing filler loading. The highest value is obtained with the gum compound. However, with increasing DSA the difference between the filled vulcanizates and the gum compound is minimized as on the one hand, gum does not show a strong strain dependence, and on the other hand, the $\tan \delta$ of loaded rubber increases rapidly with DSA up to a strain amplitude of about 20-30% DSA in this particular case. For highly loaded vulcanizates $\tan \delta$ is even higher than that of its unfilled counterpart at high DSA. Such an observation would also be related to the filler network. At 0°C , this solution SBR is in its transition zone where the polymer energy loss of polymer per-se is high due to its high viscosity, hence long relaxation time. For the filled rubber, under a strain amplitude which cannot break the filler network, the polymer fraction will be reduced so that $\tan \delta$ would be lower. When the strain amplitude increases to such an extent that a certain amount of the filler agglomerates can be broken down, the polymer trapped in this associates would be released to take part in the energy dissipation process, thus resulting in higher $\tan \delta$. Moreover, under this condition, cyclic disruption and reformation of the filler network would also impart additional energy dissipation to the filled composite. As these two processes increase with strain amplitude, $\tan \delta$ would increase steeply with DSA. As a consequence, for the highly loaded vulcanizates, $\tan \delta$ is even higher than that of gum rubber at high strain amplitudes.

It is also noted that $\tan \delta$ of the vulcanizates at high strain amplitude drops drastically with DSA. While this would be attributed to the reduction of filler network reformation at high DSA as discussed before, the longer relaxation time of polymer at low temperature would also be responsible for the lower hysteresis as the polymer chains are unable to adjust their conformations in a time scale related to both the dynamic frequency and the strain amplitude. This also applies to the $\tan \delta$ at high temperature but its effect may be minor in comparison with the filler network contribution to the hysteresis.

Comparison of different types of fillers

As mentioned previously, silica can form stronger and more developed agglomerates which would be reflected in loss tangent. This is clearly shown in Figure 9. At 70°C, while at low loading the $\tan \delta$ does not change drastically with strain amplitude, at loading higher than 20 phr, the $\tan \delta$ increase continuously without reaching a maximum over the range of DSA investigated. It is also observed that at low strain amplitude, the highly loaded rubbers, relative to vulcanizate having 30 phr silica, give lower hysteresis at low strain amplitude but at high strain amplitude $\tan \delta$ is higher, with a crossover at DSA around 10%. Such an observation can also be explained based on the strength and development of filler agglomeration. As silica can form stronger filler agglomerates, at low strain amplitude, they are unable to be disrupted and lower hysteresis would be expected. When high strain amplitude is applied, more agglomerates will breakdown and reform, resulting in higher hysteresis. The agglomerates are so strong and so developed that at the strain amplitude that the carbon black network is mostly destroyed, a great portion of agglomerates is still involved in an energy dissipation process. The fact that the higher hysteresis at low strain amplitude of 30 phr silica compound and its low increase rate with increasing DSA indicates that the concentration of weak agglomerates is higher and that of stronger ones is lower, compared to its highly loaded counterparts.

At 0°C, it is observed that over the DSA range investigated, $\tan \delta$ decreases when the filler loading increases. Compared with carbon black-filled rubber, the maximum $\tan \delta$ appears at higher strain amplitudes and the overall $\tan \delta$ is substantially lower, especially for the highly loaded vulcanizates. All these features of the silica compounds are mainly

and undoubtedly due to their strong filler network, resulting in reduction of the polymer fraction and less filler agglomerates being able to be broken down and reformed under the strain amplitude applied.

The arguments about the role of filler network on dynamic hysteresis can be further strengthened by the results of CSDPF which are shown in Figure 10. The lower $\tan \delta$ over the entire range of DSA at high temperature, the higher $\tan \delta$ at low strain amplitude, and lower values at larger strain of CSDPF-filled vulcanizates relative to their carbon black counterparts, are primarily due to the fewer and weaker agglomeration of the filler aggregates. This phenomenon is significantly enhanced by TESPT modification of CSDPF (Figure 11).

Temperature dependence of loss tangent

The evidence of the impact of filler agglomeration to the dynamic properties can also be reinforced by temperature dependence of $\tan \delta$ obtained from temperature sweeps.

As shown in Figure 12, the silica compounds are quite distinctive in their temperature dependence of loss factors. Relative to the carbon black vulcanizates, the very low $\tan \delta$ of the silica compounds over the temperature range from -30 to 40°C is certainly associated with the feature of more and stronger filler agglomerates with a large volume of trapped rubber unable to participate energy dissipation, even though the real volume fraction of polymer is higher from the silica density point of view. On the other hand, the stronger filler network would also result in depressing another energy dissipation process involving disruption and reformation of filler network. Obviously the increase of $\tan \delta$ with temperature represents the increase in the network portion which involves internal friction. This portion augments continuously reaching a maximum in the range of the temperature in the region from 75 to 85°C, indicating the network is more developed and/or stronger than that of the carbon blacks. Consequently, for the silica-filled rubber, there seems to be two peaks in the $\tan \delta$ -temperature curve: one is related to polymer, the other corresponds to a filler network in which polymer-filler interaction hence mobility of polymer segments is also involved.¹⁸ Depending on the number and strength of the

agglomerates, these two peaks may be distinctly separate as in the silica case, or merged together, leading to a broad peak, as in the case of carbon black.

Accordingly, the low filler-filler interaction hence less and weaker filler network of CSDPF manifests itself primarily in a $\tan \delta$ -temperature curve featured by high hysteresis at low temperature, lower hysteresis at high temperature, with a narrower peak in the polymer transition zone. As observed in the strain sweep, this phenomenon can be further developed by TESPT modification (Figure 12).

To sum up, for a given polymer system, filler networking plays a critical role in determining the dynamic properties of the filled rubber, hysteresis in particular. Its roles can be summarized as follows:

- To the extent that the filler network cannot be broken down under the applied deformation, the formation of filler network would substantially increase the effective volume fraction of the filler due to the rubber trapped in the agglomerates, leading to high elastic modulus and low hysteresis.
- The breakdown and reformation of the filler network would cause an additional energy dissipation hence higher hysteresis during cyclic strain would be expected.
- In the transition zone of the polymer at low temperature where the main portion of the composite for energy dissipation is polymer matrix, and the filler network may not be easily broken down, the hysteresis may be significantly attenuated, by the filler networking due to the reduction of the effective volume of the polymer.
- Also in the transition zone, once the filler network can be broken down and reformed under a cyclic deformation, the hysteresis can be substantially augmented through release of polymer to participate in energy dissipation and change in the network structure.

Accordingly, besides the hydrodynamic effect, the necessary conditions for high hysteresis of filled rubber, among others, are presence of filler network, and breakdown and reformation of the network under dynamic strain. Practically, a good balance of $\tan \delta$ at different temperatures with regard to tire tread performance, namely higher hysteresis at low temperature and low hysteresis at high temperature, can be achieved by depressing filler network formation.

CONCLUSION

Filler aggregates in a polymer matrix have a tendency to form a filler network. During dynamic strain, if the filler network cannot be broken down, the elastic modulus would increase substantially due to the rubber trapped in the network. The trapped rubber can be estimated with Van der Poel theory. It was found that the amount of trapped rubber increases with filler loading and decreases with increasing strain amplitude. Temperature also has a significant impact. The breakdown and reformation of the filler network, which may release the trapped rubber for energy dissipation, would cause an additional energy dissipation process, imparting higher hysteresis to the- filled rubber. Compared to carbon black, silica is able to form a stronger and more developed filler network resulting in higher modulus and lower hysteresis at low temperature. The reverse effect was observed for CSDPF, especially for its TESPT modified counterpart, i.e., these fillers show less tendency to form a filler network, giving lower hysteresis at high temperature and higher hysteresis at low temperature.

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Dr. K. Mahmud for his support of this work. Special thanks are due to R. E. Dickinson for his assistance in planning and carrying out the compounding. Thanks are also extended to Cabot Corporation for permission to publish the paper.

REFERENCES

1. A. R. Payne, in "Reinforcement of Elastomers", G. Kraus Ed., Interscience Publishers, New York, 1965, Ch. 3.
2. A. R. Payne and R. E. Whittaker, *Rubber Chem. Technol.*, **44**, 440 (1971).
3. A. I. Medalia, *Rubber Chem. Technol.*, **51**, 437 (1978).
4. J. R. S. Warring, *Trans. Inst. Rubber Ind.*, **26**, 4 (1950).
5. A. R. Payne, *J Polym. Sci.*, **6**, 57 (1962).
6. A. R. Payne, *Rubber Plast Age*, Aug. 1963, (1961).
7. E. Guth, R. Simha, and O. Gold, *Kolloid Z.*, **74**, 266 (1936).
8. E. Guth and O. Gold, *Phys. Rev.*, **53**, 322 (1938).
9. E. Guth, *J Appl Phys.*, **16**, 20 (1945).
10. A. I. Medalia, *Rubber Chem. Technol.*, **45**, 1171 (1972).
11. A. I. Medalia, *J Colloid Interf. Sci.*, **24**, 393 (1967).
12. S. Wolff, and J. -B. Donnet, *Rubber Chem. Technol.*, **63**, 32 (1990).
13. C. van der Poel, *Rheologica Acta*, **1**, 198 (1985).
14. M. -J. Wang, S. Wolff and J. -B. Donnet, *Rubber Chem. Technol.*, **64**, 559 (1991).
15. M. -J. Wang, S. Wolff and J. -B. Donnet, *Rubber Chem. Technol.*, **64**, 714 (1991).
16. S. Wolff and M. -J. Wang, *Rubber Chem. Technol.*, **65**, 329 (1992).
17. M. -J. Wang, S. Wolff and E. -H. Tan, *Rubber Chem. Technol.*, **66**, 178 (1993).
18. M. -J. Wang, *Rubber Chem. Technol.*, in press.
19. A. R. Payne, *Rubber J*, **146**, 36 (1964).
20. G. Kraus, *J. Appl. Polymer Sci., Appl. Polymer Symposium*, **39**, 75 (1984).
21. Wolff and M. -J. Wang, in "Carbon Black, Science and Technology", J. -B. Donnet, R.C. Bansal and M. -J. Wang Eds, Marcel Dekker, Inc., New York, 1993, Ch. 9.

FIGURE CAPTIONS

- Figure 1. Strain dependence of G' at 70 and 0°C and 10 Hz for SSBR compounds with different loading of carbon black N234.
- Figure 2. G'/G'_{gum} measured at different strain amplitudes at 70 and 0°C and 10 Hz for N234 filled SSBR compounds as function of filler concentration. The effective filler volume used for plotting is derived from the data at 5% DSA.
- Figure 3. G'/G'_{gum} as a function of effective filler volume for a variety of filler and Van der Poel filler volume- G'/G'_{gum} plot.
- Figure 4. Schematic presentation of effective volume of filler ϕ_{eff} ($f\phi$, equation 3) and Van der Poel effective volume ϕ_{VdP} .
- Figure 5. Strain dependence of G' at 70 and 0°C and 10 Hz for SSBR compounds with 50 phr different fillers.
- Figure 6. Strain dependence of G'' at 70 and 0°C and 10 Hz for SSBR compounds with different loading of carbon black N234.
- Figure 7. Strain dependence of G'' at 70 and 0°C and 10 Hz for SSBR compounds with 50 phr different fillers.
- Figure 8. Strain dependence of $\tan \delta$ at 70 and 0°C and 10 Hz for SSBR compounds with different loading of carbon black N234.
- Figure 9. Strain dependence of $\tan \delta$ at 70 and 0°C and 10 Hz for SSBR compounds with different loading of silica.
- Figure 10. Strain dependence of $\tan \delta$ at 70 and 0°C and 10 Hz for SSBR compounds with different loading of CSDPF.
- Figure 11. Strain dependence of $\tan \delta$ at 70 and 0°C and 10 Hz for SSBR compounds with different loading of MCSDPF.
- Figure 12. Temperature dependence of G'' at 70 and 0°C and 10 Hz for SSBR compounds with 50 phr different fillers.

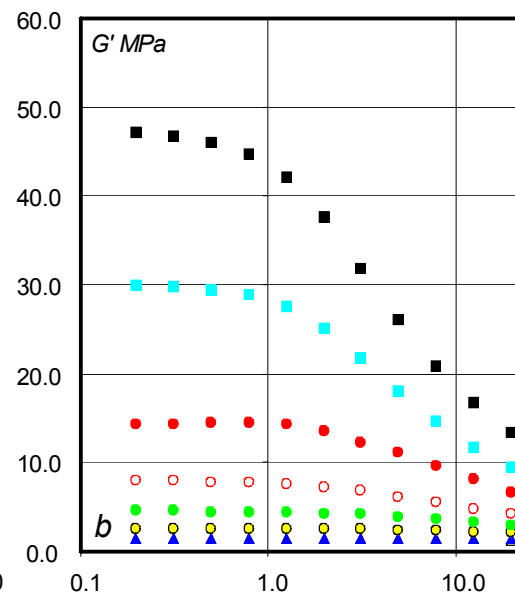
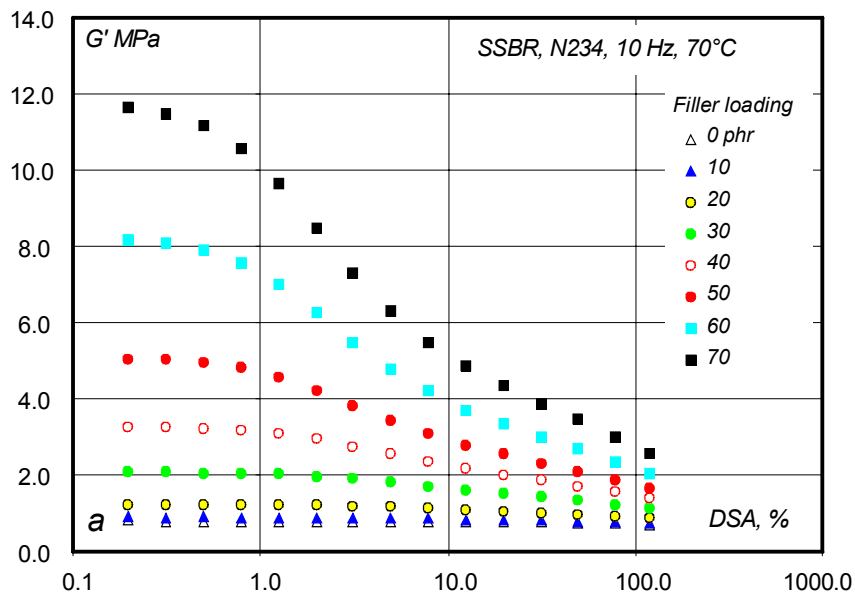


Figure 1

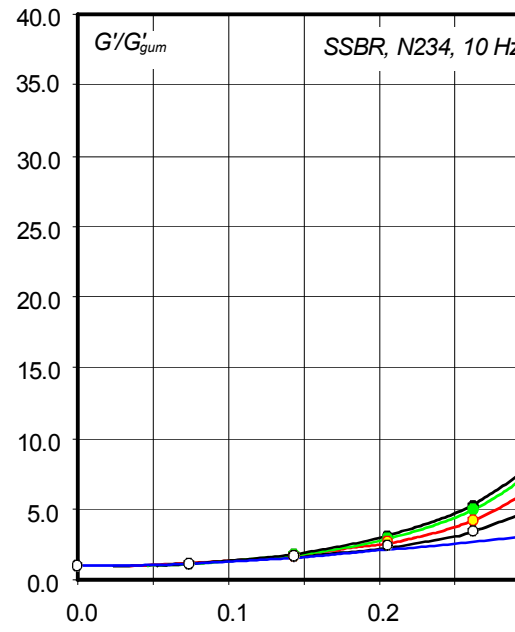
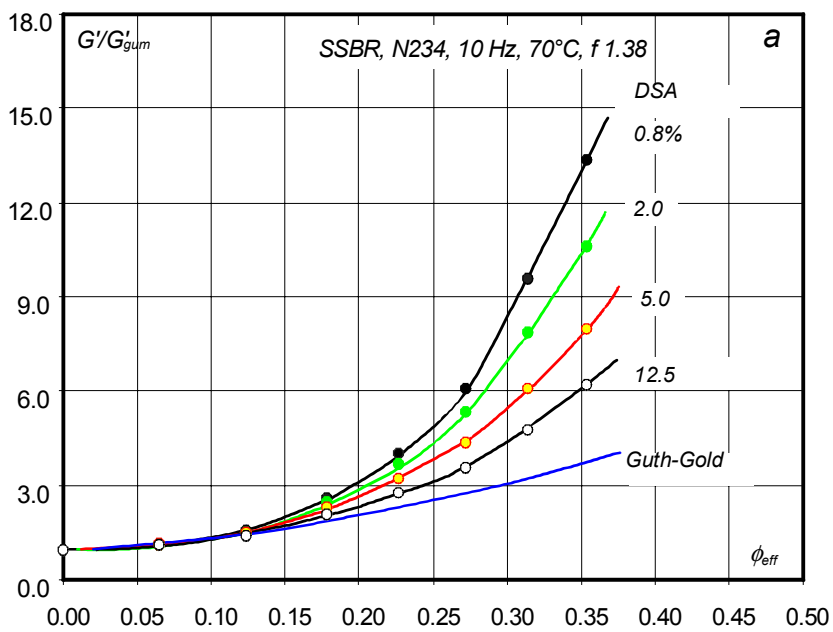


Figure 2

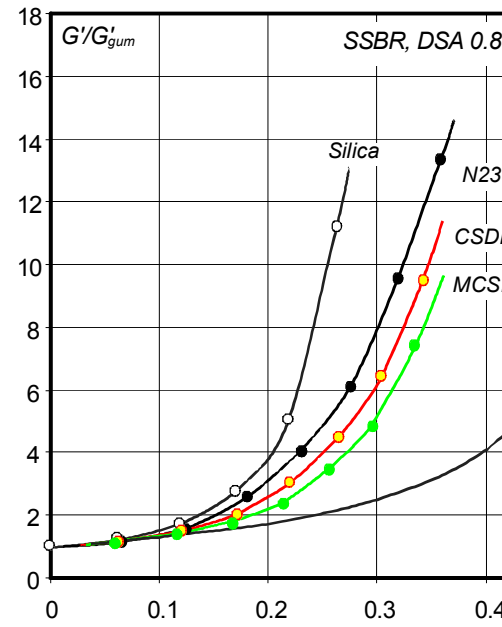
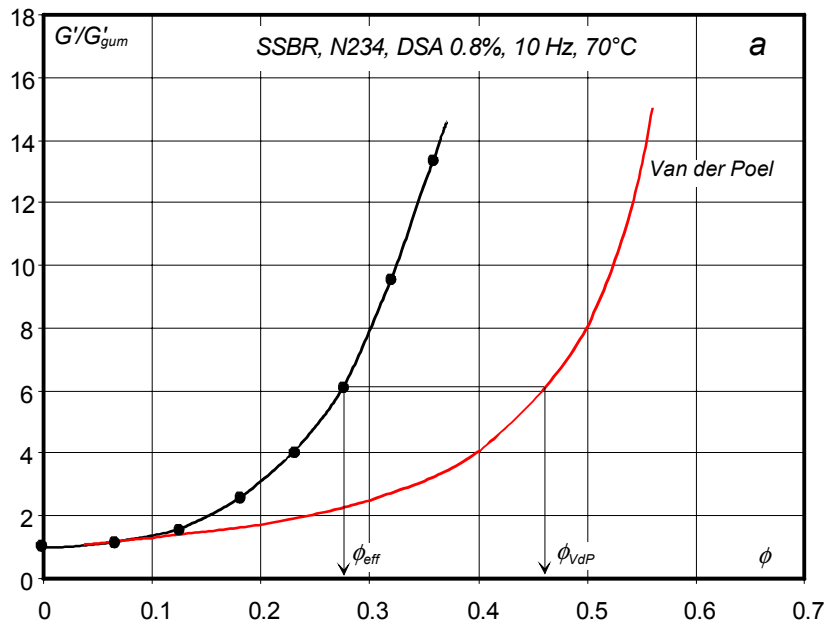
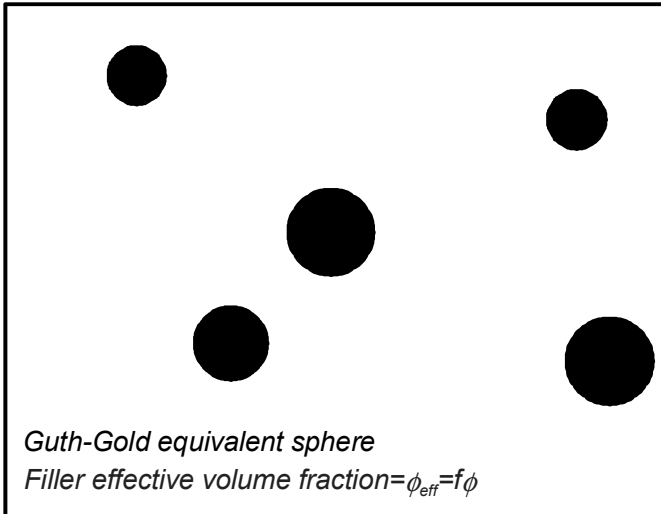
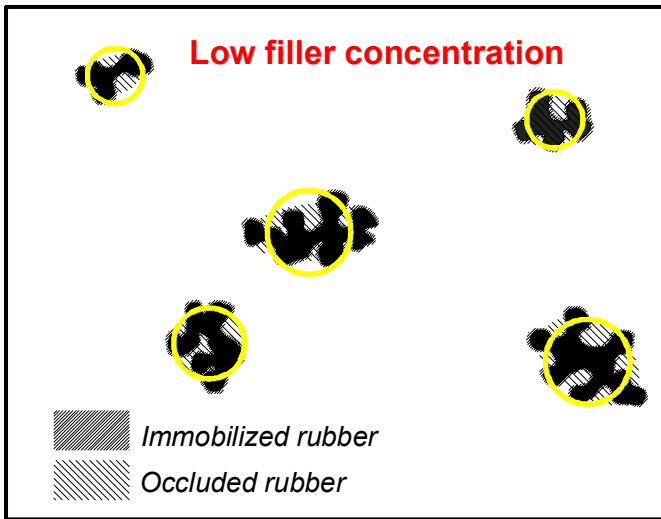
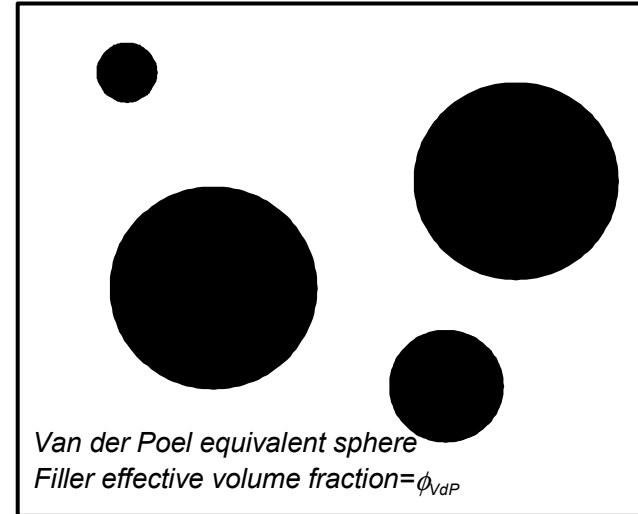
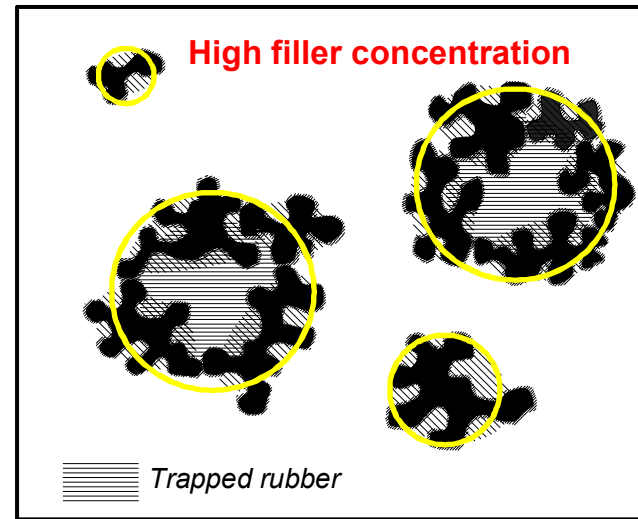


Figure 3



a



b

Figure 4

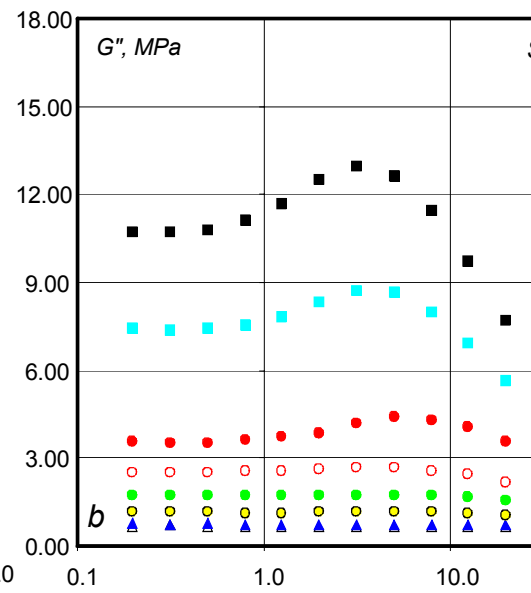
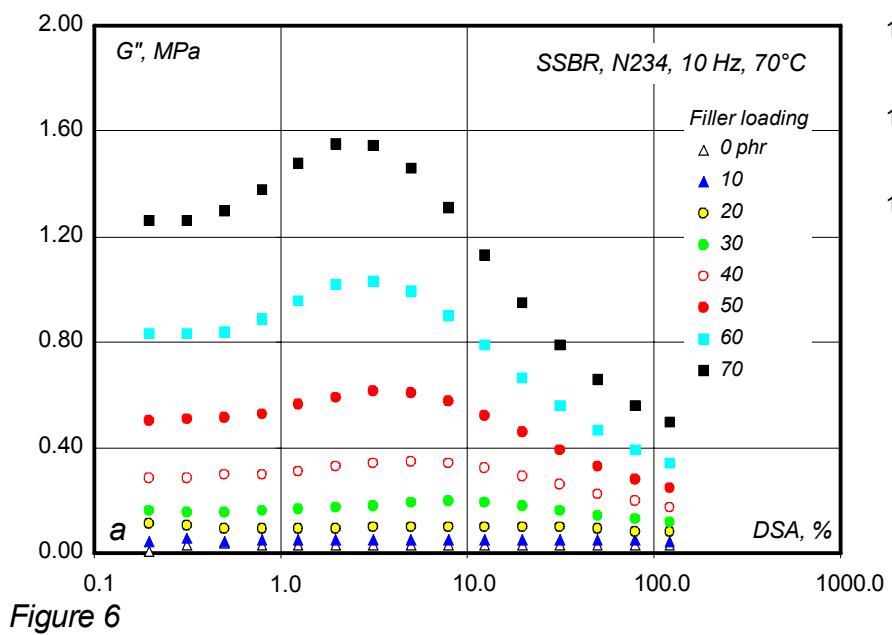


Figure 6

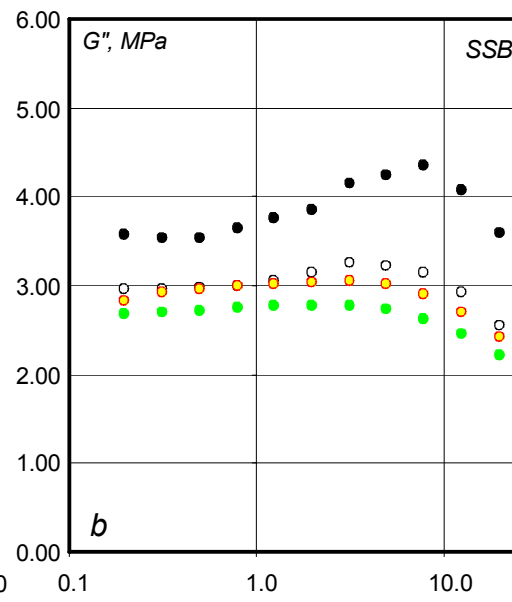
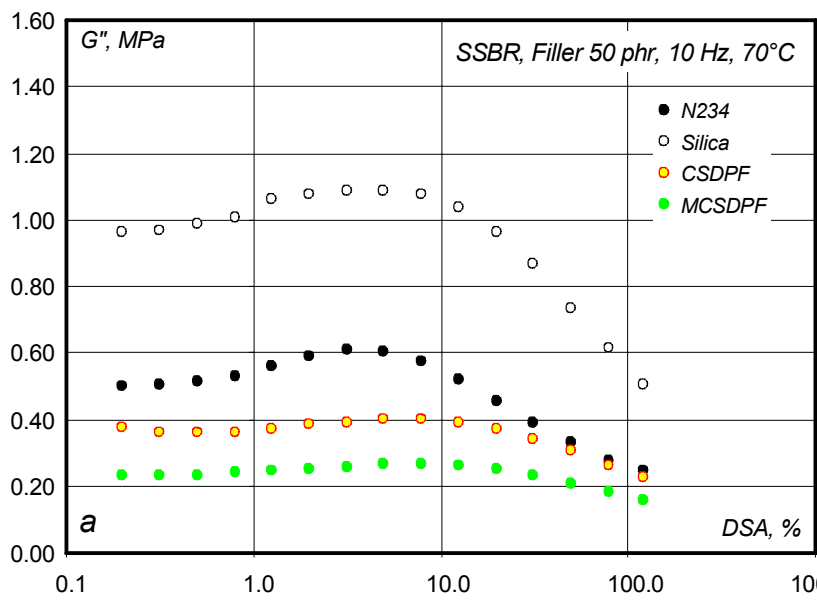


Figure 7

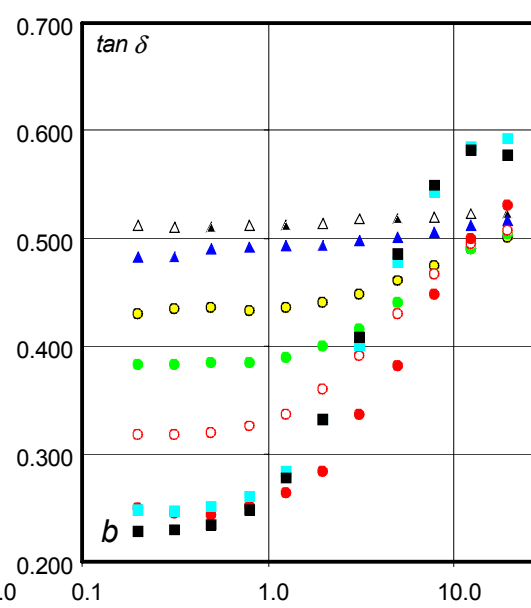
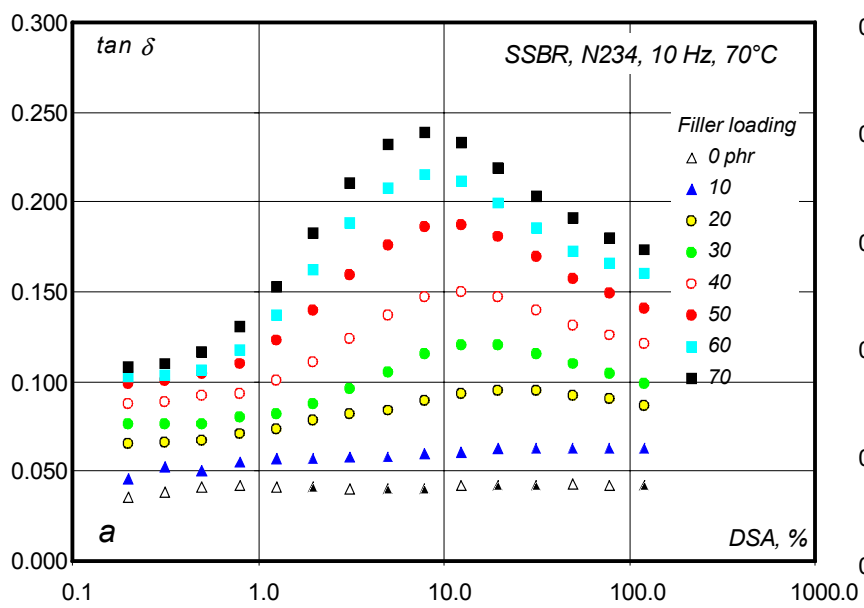


Figure 8

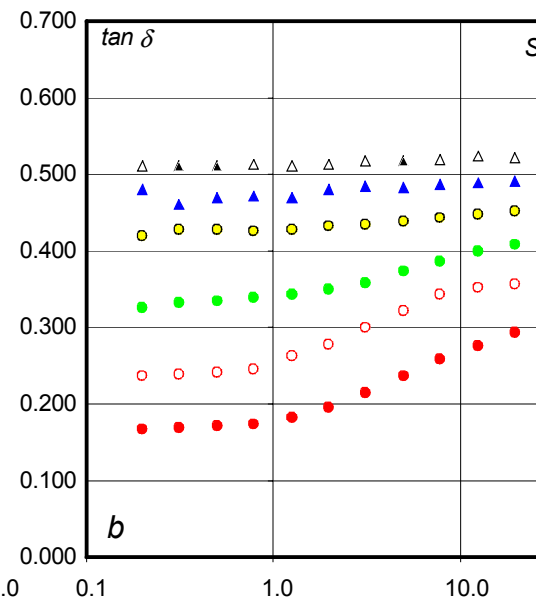
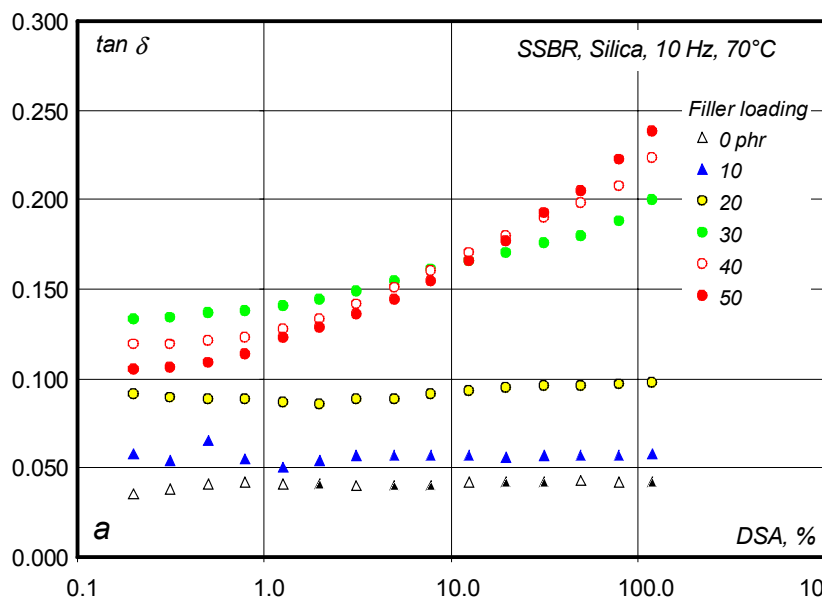


Figure 9

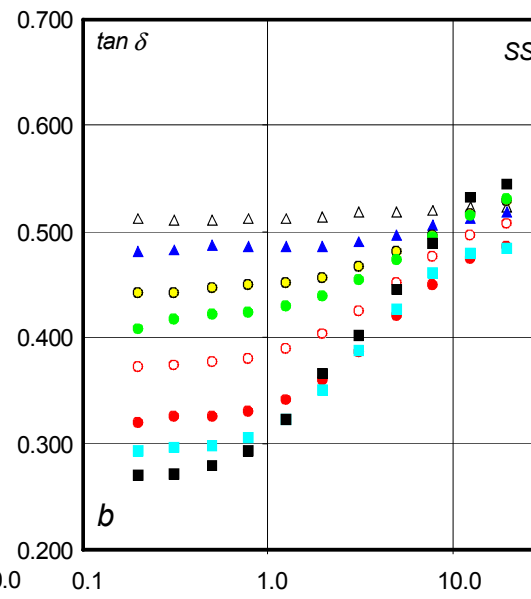
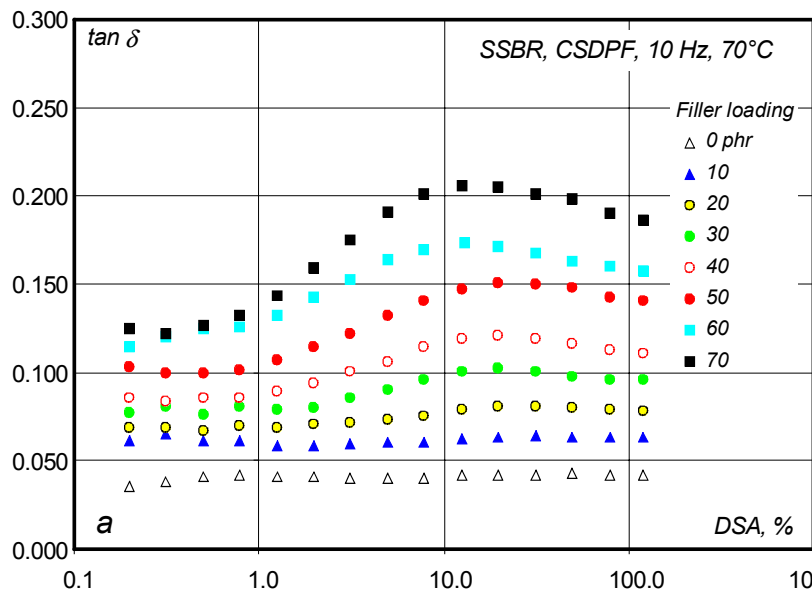


Figure 10

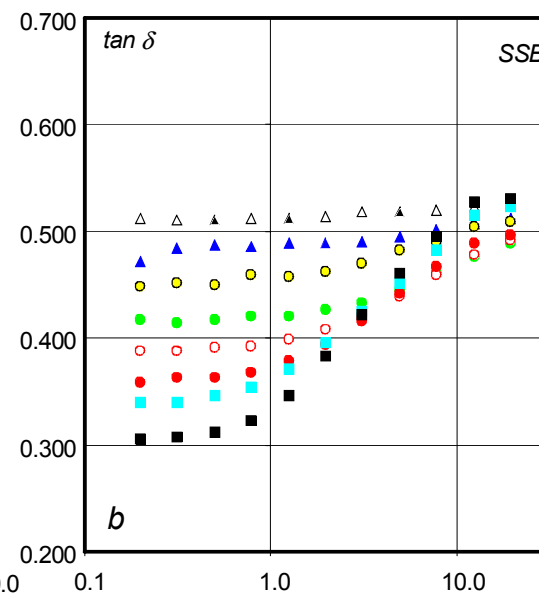
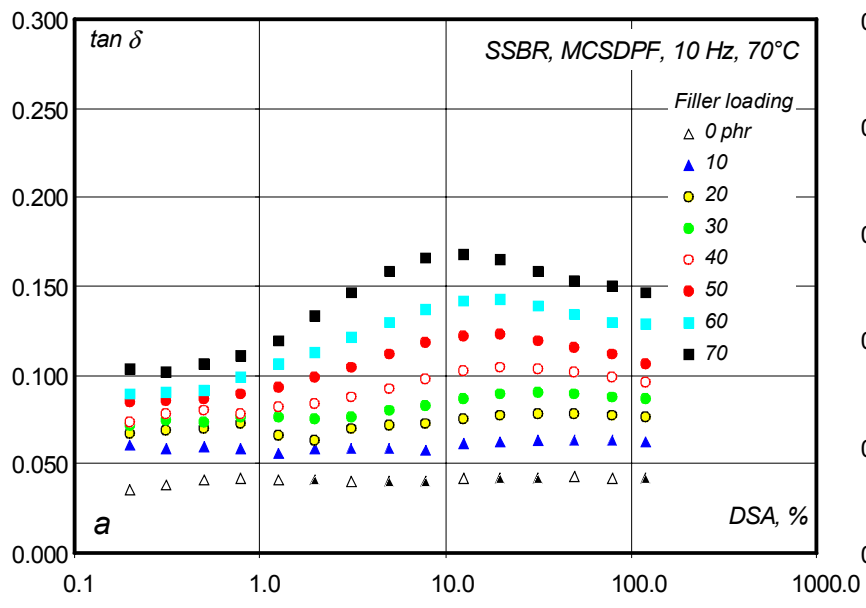


Figure 11

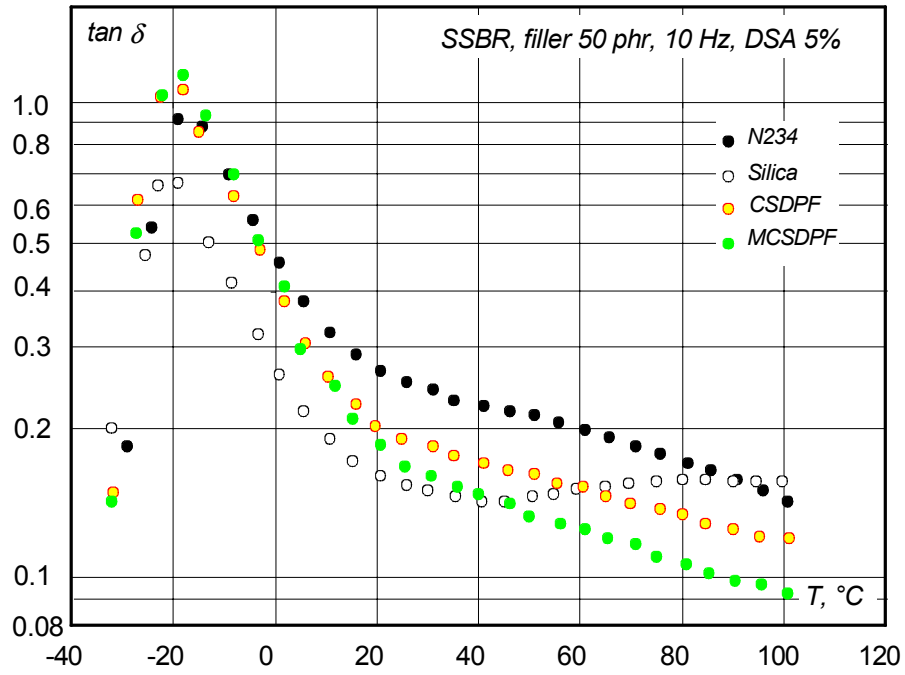


Figure 12

Table I. Analytical Properties of Fillers

<i>Filler</i>	<i>Si</i> <i>(ash analysis), %</i>	<i>Surface area,</i> <i>m²/g (N₂)</i>	<i>Surface area,</i> <i>m²/g (t-area)</i>	<i>CDBP,</i> <i>cL/100g</i>
<i>Carbon black N234</i>	0.03	123.3	120.5	100.7
<i>CSDPF</i>	4.7	175.0	122.4	101.8
<i>Silica</i>	NA	150	NA	NA

Table 2. Formulation

<i>Polymer</i>	100
<i>Filler</i>	Variable
<i>TESPT</i>	Variable
<i>Zinc oxide</i>	3
<i>Stearic acid</i>	2
<i>Antioxidant Flexzone 7P^a</i>	1
<i>CBS^b</i>	1.25
<i>MBT^c</i>	0.2
<i>Sulfur</i>	1.75

- a. Antioxidant, *N*-(1,3-dimethyl butyl)-*N'*-phenyl-*p*-phenylene diamine.
b. Accelerator, *N*-cyclohexyl-2-benzothiazole sulphenamide.
c. Accelerator, 2-mercaptobenzothiazole.

Table III. Var der Poel Equivalent Filler Volume ϕ_{VdP}

<i>Filler loading, phr</i>	<i>DSA, %</i>	<i>Temperature, °C</i>	<i>N234</i>	<i>Silica</i>	<i>CSDPF</i>	<i>MCSDPF</i>
70	0.8	70	0.552	-	0.520	0.483
50	0.8	70	0.462	0.538	0.415	0.371
30	0.8	70	0.315	0.330	0.240	0.200
70	5.0	70	0.500	-	0.478	0.458
50	5.0	70	0.410	0.520	0.382	0.345
30	5.0	70	0.278	0.290	0.235	0.192
70	0.8	0	0.620	-	0.578	0.552
50	0.8	0	0.523	0.540	0.455	0.430
30	0.8	0	0.342	0.365	0.290	0.280
70	5.0	0	0.576	-	0.530	0.518
50	5.0	0	0.495	0.523	0.430	0.408
30	5.0	0	0.310	0.360	0.275	0.260