

Effect of Filler Network on Dynamic Viscoelastic Properties of Uncured Polymethylvinylsiloxanes Filled with Silica and Carbon Black

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ABSTRACT: Dynamic properties of polymethylvinylsiloxane (PMVS) filled with filler-blends composed of carbon black (CB) and silica (SiO₂) were investigated using an advanced rheometric expansion system. A variety of weight fraction of CB to SiO₂ were 0/100, 10/90, 30/70, 50/50, 70/30, 90/10, and 100/0, and a bifunctional organosilane, bis(3-triethoxysilylpropyl)tetrasulfane, was used to facilitate the filler dispersion. The results reveal that the incorporation of CB/SiO₂ filler-blends into PMVS result in a reduced *Payne effect*. This effect reaches a minimum when the ratio of CB/SiO₂ approaches 1, and then it began to rebound with

the ratio increase. Meanwhile, a characteristic Newtonian viscosity plateau appearing in low frequencies also significantly decreases, depending on the amount of CB or SiO₂ added. On the basis of a simplified Fowke model, we ascribe this phenomenon to the deteriorated filler network, which is predominantly induced by the totally different surface activity between CB and SiO₂. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3477–3482, 2006

Key words: dynamic properties; silica; carbon black; filler network; polymethylvinylsiloxane

INTRODUCTION

Among the fillers that have been used for reinforcing elastomers, carbon black (CB) and silica (SiO₂) have become the most important additives that can endow rubber-like products with many desirable properties, such as modulus, tensile strength, abrasion, resistance, etc.¹ It is well known that CB possesses high surface area and high surface activity, and consequently has become a preferred filler for various types of tires; compared with CB, SiO₂ shows a strong tendency to agglomerate due to densely covered silanol groups, leading to a poor compound processability. Through surface modification of SiO₂ by using silane coupling agents, the dispersion of it can be significantly improved, but the SiO₂/silane system remains rather more expensive. Hence, it only serve as a minor portion of the filler in rubber applications, especially in off-the-road tire treads, for enhancements of tear resistance, cut growth, and adhesion properties.

Over the last years, the everlasting demands for reduction in fuel consumption and lowering of gas emission have promoted people to seek for proper fillers for the increase in wear resistance, the reduction in rolling resistance, and improvement in wet skid resistance^{2–4} More recently, addition of CB in combination with surface-modified SiO₂ for compromising these aforementioned aspects has been increasingly adopted as functional additives to endow further optimization of tread properties for a range of service conditions.⁵ A newly designed filler material, referred to as CB–SiO₂ dual phase filler (CSDPF), has been commercialized, and applied satisfactorily to improve the tradeoff between rolling resistance and wear resistance CB.²

It is well accepted that the dynamic viscoelastic properties are very important in academic research and commercial application for polysiloxane materials.⁶ To our knowledge, few studies concerning these aspects have been reported up to date.^{3,7} The objective of the present article is to investigate the effect the filler-blends composed of CB and SiO₂ on the dynamic properties of polymethylvinylsiloxane (PMVS). The interaggregate interactions and the variations of filler network caused by CB–SiO₂ filler-blends in the filled composites are discussed in detail.

EXPERIMENTAL

Materials and samples preparation

The PMVS samples were commercially available products ($M_w = 600,000$, $M_n = 465,000$). The CB

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TABLE I
Typical Properties of CB and SiO₂

Property	Silica	Carbon black
N ₂ (BET) surf. area (m ² /g)	280	80
Elementary particle diameter (nm)	20	40
DBP adsorption (mL/100 g)	224	102
CTAB ads. surf. area (m ² /g)	126	82
pH (4% suspension in H ₂ O)	6.7	9.2

(N330[®]) was supplied by Hangzhou Fuchunjiang Chemical, China, while SiO₂ was synthesized following a conventional sol-gel process⁸ (Table I). A bifunctional organosilane, bis(3-triethoxysilylpropyl)tetrasulfane (TESPT), was used to facilitate filler dispersion (Scheme 1), which was proved to be strongly effective and efficient.⁴

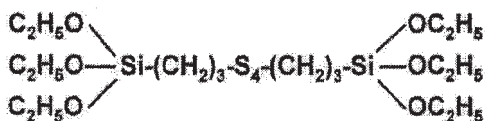
The mixing of the compounds was carried out in a two-roll mill at room temperature, following a prescription as shown in Table II, and a mixing procedure as given in Table III.

Dynamic viscoelastic properties measurements

The dynamic viscoelastic properties of PMVS/filler-blends unvulcanizates were measured on an advanced rheometric expansion system (ARES), in the model of dynamic strain sweep and dynamic frequency (ω) sweep, using disc specimens with a thickness of 1.8 mm and a diameter of 25 mm. For the strain sweep, the test was conducted with a frequency of 10 rad/s by varying the strain from 0.01 to 100%; and for the frequency sweep, the test was performed within the frequency range from 100 to 0.01 rad/s under a constant strain of 0.06%.

Bound rubber (BR) measurements

The procedure for a measurement of bound rubber content used in the present study was based on the method as given in ref. 9. The small pieces of about 2 g of filled compounds were immersed in 25 mL toluene for 7 days at room temperature. After extraction, the rubber-silica gel was dried in an oven at 70°C until the sample weight approached constant. The percentage of the BR content was calculated according to the following equation



Scheme 1 TESPT.

TABLE II
Formulations for PMVS Filled with CB and SiO₂ Blends

PMVS	100
Silica	variable ^a
Carbon black N330	Variable ^b
Coupling agent TESPT	2 ^c
Diphenyl silandiol	3
Dicumyl peroxide (DCP)	1.8
Liquid paraffin	1.5

^a The total amounts of CB and SiO₂ were set fixed at 60 phr.

^b The percentage ratio of CB/SiO₂ was set as following: 0/100, 10/90, 30/70, 50/50, 70/30, 90/10, and 100/0, respectively.

^c TESPT was added with the filler-blends during the early stage of mixing.

$$R_B = \frac{W_{fg} - W[m_f/(m_f + m_p)]}{W[m_f/(m_f + m_p)]} \times 100 \quad (1)$$

in which W_{fg} is the weight of silica-rubber gel, m_f is the weight of filler in the compound, m_p is the weight of polymer in the compound, and W is the weight of the specimen tested.

RESULTS AND DISCUSSION

Figure 1 presents plots of dynamic storage modulus (G') versus strain measured at 25°C and 10 rad/s for the (CB-SiO₂) fillers filled PMVS. It is obvious that in all cases, a linear viscoelastic behavior corresponding to strain-independent dynamic storage modulus G' can be observed at small strain. Upon reaching critical strain amplitude, the curves drop sharply with an obvious decreasing G' value. In general, a remarkable decrease in G' at critical strain amplitude is attributed to the existence of a filler network in elastomer matrix and is referred to as "Payne effect."^{10,11} It is believed that filler network is formed directly through filler-filler interactions and indirectly through polymer chains bridging two different particles or entanglements of different polymer chains adsorption onto two adjacent particles. Hence, the G' at critical strain amplitude reflects the strength and stability of filler network. Additionally, it is worth noting that with the increasing amount of CB in the filler-blends from 0 to 100%, the strain-dependent G' at small strain initially

TABLE III
Mixing Procedures

0''	PMVS
30''	Diphenyl silandiol
1'	Filler and coupling agent
6'	Oil and paraffin
9'	Dicumyl peroxide
12'	Dumping

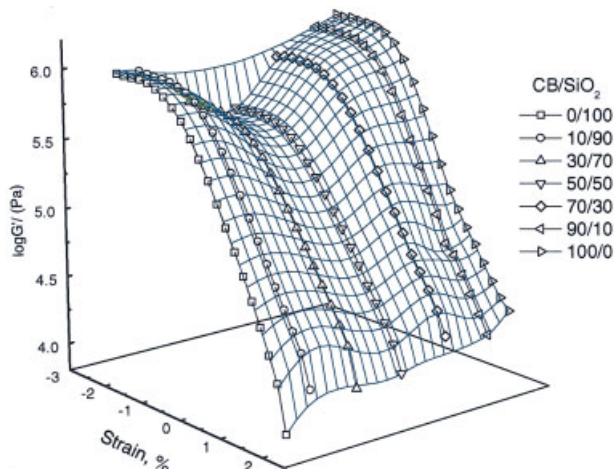


Figure 1 Strain dependence of G' at 25°C and 10 rad/s for PMVS filled with CB/SiO₂ blends of various ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

shows a decreasing tendency, and after passing through a minimum at the CB–SiO₂ ratio of 50/50, it begins to rebound back quickly, namely the *Payne effect* experiences a decrease–increase transformation with varying compositions in the filler-blends. This confirms that *Payne effect* is closely related to filler–filler interactions, and adding two kinds of filler into PMVS will lead to a deteriorated filler network, regardless of the filler type.

Figure 2 gives dynamic loss modulus (G'') as a function of strain over the range from 0.01 to 1 for the samples with a variety of CB/SiO₂ ratios in the filler-blends. Similar to G' , the G'' value remains constant until the strain reaches critical amplitude, then it decreases suddenly, exhibiting a phenomenon character-

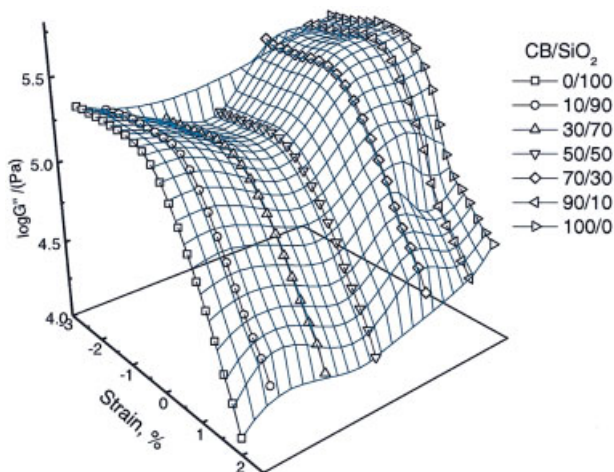


Figure 2 Strain dependence of G'' at 25°C and 10 rad/s for PMVS filled with CB/SiO₂ blends of various ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

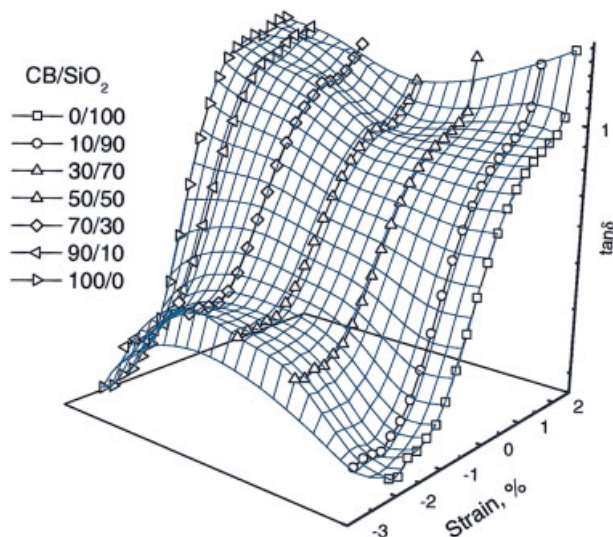


Figure 3 Strain dependence of $\tan \delta$ at 25°C and 10 Hz for PMVS filled with CB/SiO₂ blends of various ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ized by *Payne effect*. Upon the ratios of CB/SiO₂ in the filler-blends approaching 1, it can be observed that the amplitude of strain-independent G'' in the small strains decreases significantly, which accords well with that of G' in Figure 1. If G' is mainly related to filler network that is reduced during dynamic strain, G'' is regarded¹⁰ to be substantially controlled by the breakdown and reformation of the filler network. On the basis of this idea, we propose that the addition of CB and SiO₂ filler-blends have partially disrupted the CB or SiO₂ filler network formed originally, resulting in a decreased *Payne effect* or a imperfectly developed aggregates structure. Therefore, the reformation capability of aggregates structure is disrupted, leading to a lower G'' value.

Figure 3 presents the strain dependence of loss tangent ($\tan \delta$) at 25°C and 10 rad/s for CB–SiO₂ filled unvulcanizates. It can be seen that $\tan \delta$ increases slowly upon increasing strain amplitude within a short range (<0.1%) and after that there is an upsurge, indicating the breakdown of the filler network. It is also noted that, when the ratio of CB to SiO₂ approaches 1, the strain-dependent $\tan \delta$ reaches a maximum value. We ascribe this variation to the reducing filler network structure in the PMVS/filler-blends systems. As $\tan \delta$ is the ratio of G'' to G' (where G' is mainly related to filler network and G'' related to the breakdown and reformation of these structures), the change in $\tan \delta$ by varying strain amplitude would reflect the ratio of these processes, and a higher $\tan \delta$ in the initial stage would mean a weakly formed filler network. However, this network will easily break down, leading to relatively a higher energy loss.

Figure 4 shows a plot of G' versus ω measured at 25°C and 10 Hz. As can be seen that in the higher ω

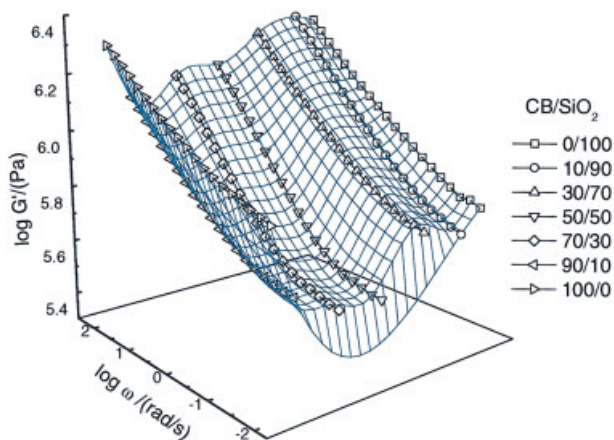


Figure 4 Frequency dependence of $\log G'$ at 25°C and 10 Hz for PMVS filled with CB/SiO₂ blends of various ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

range, G' decreases linearly with decreasing ω for all samples, following the equation of $\log G' \sim 2\log \omega$, given by the linear viscoelastic theory.¹² However, in the lower ω range, the linear viscoelastic behavior disappears, and the CB-SiO₂/PMVS compounds display an extraordinary ω -independent rheological behavior. According to our previous work,¹² the Newtonian viscoelastic plateau in the terminal region can be attributed to the existence of filler network and the G'' value in the plateau reflects the level of filler network formation. Hence, this Newtonian plateau in relation to the filler network is progressively decreasing as the ratio of CB/SiO₂ is set closing to 1, indicating further agreements with the observations in Figures 1 and 2.

Figure 5 presents G'' as a function of ω for the composites with different CB-SiO₂ compositions. All

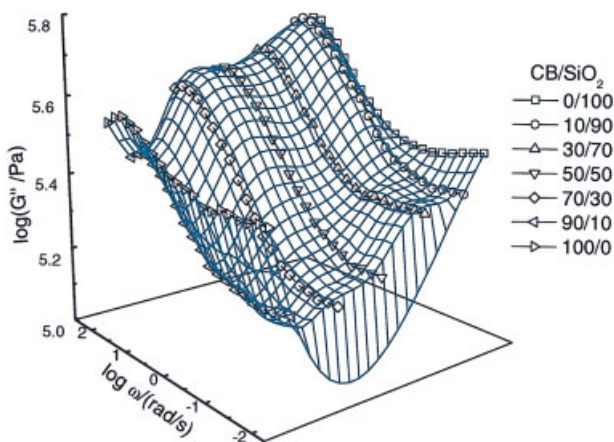


Figure 5 Frequency dependence of $\log G''$ at 25°C and 10 Hz for PMVS filled with CB/SiO₂ blends of various ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

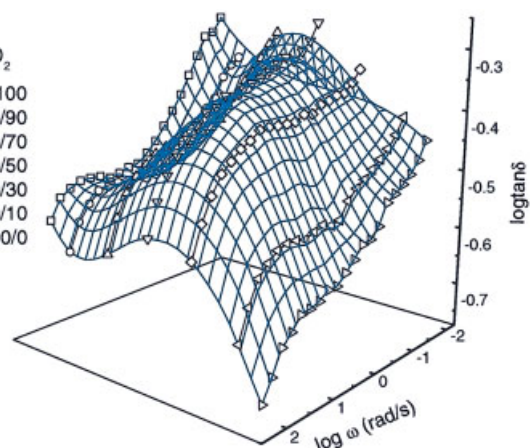


Figure 6 Frequency dependence of $\log \tan \delta$ at 25°C and 10 Hz for PMVS filled with CB/SiO₂ blends of various ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the samples show varying tendencies upon decreasing ω similar to those as given in Figure 4, especially in the lower ω range. It is noted that when the CB/SiO₂ ratio is 50/50, the CB-SiO₂/PMVS system exhibits the lowest Newtonian viscoelastic plateau. This phenomenon can also be ascribed to the resultant formation and its variations of agglomerated or network structure of filler CB and SiO₂. For the samples with differential CB-SiO₂ ratios, the decreasing G'' value in the terminal ω region is responsible for a poor CB-SiO₂ aggregates network.

Figure 6 gives the plots of $\tan \delta$ versus ω for the composites with various CB/SiO₂ ratios. Similar to the results in Figure 3, in the low ω range, $\tan \delta$ shows relatively higher value when the filler CB/SiO₂ ratio approaches 1. It is well known that in polymer rheology $\tan \delta$ is representative of energy loss or dynamic hysteresis. As far as dynamic relaxation is concerned, a higher $\tan \delta$ in the low ω range is apparently related to a loosely formed filler network.

BR (%) is the rubber portion that can no longer be separated from the filler when the rubber batch is extracted in a good rubber solvent (such as toluene) over a specified period of time at room temperature. The formation of BR involves physical adsorption, chemisorption, and mechanical interaction and is unanimously believed as the macroscopic result of rubber-filler interactions.¹ It can be seen from BR versus CB/SiO₂ ratio as plotted in Figure 7 that, with the increasing amount of CB in the filler-blends from 0 to 100%, the content of BR initially decreases from 0.64 down to 0.56, but after passing through a minimum at the CB-SiO₂ ratio of 50/50, it increases sharply. The variation of BR upon increasing CB content shows good agreement with the varying tendencies, as presented in Figures 1 and 4. It seems that the incorporation of another type of filler will affect the original

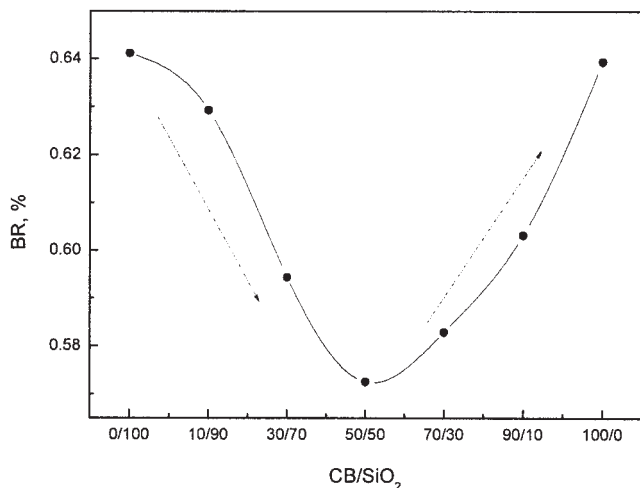


Figure 7 Plot of BR (%) versus CB/SiO₂ ratio.

filler–elastomer interactions considerably, which is not promising in relation to practical use. Furthermore, taking the formation mechanism of BR¹ into account, we believe that this result is resulted from the weakly formed filler network.

The phenomenon that a change of the CB–SiO₂ ratios in PMVS would result in an altered *Payne effect* implies that this effect is sensitive to filler network structure and its variations. Concerning the *Payne effect*, a well-accepted view is that filler agglomeration and network formation are responsible for the high levels of reinforcement, while deagglomeration and network breakdown are responsible for the nonlinearity with strain.^{9,13} The decrease of *G'* and *G''* upon increasing strain amplitude have been attributed to several mechanisms that can be sorted as (i) the destruction–reformation of a percolation network of filler involving polymer bounded to the filler, (ii) adsorption–disorption of polymeric chains at the interface, and (iii) disentanglement of bulk polymer from the rubber bounded to the surface. A direct experimental support for the *Payne effect* was recently reported from electron microscopy studies.¹⁴ Very recently, a comprehensive review of the filler agglomeration or network formation, which are well accepted and applied to clarify the generally nonlinear viscoelastic behavior of filled systems, has been published,¹⁵ in which the common features between the phenomenological agglomeration/deagglomeration Kraus approach and recent seminetworking approaches (two aggregate VTG model, links-blobs mode, and kinetically cluster–cluster aggregation) are discussed. Hence, the *Payne effect* is regarded to be indicative of the strength of filler network, and the variations of this effect pose a considerable effect on dynamical properties.

Present discussion declares the significant effects of CB/SiO₂ ratios on the *Payne effect*, and furthermore,

the filler network formed in PMVS. When the ratio of CB/SiO₂ approaches 1, there seems no discernible *Payne effect*, suggesting the existence of a continually deteriorated filler network. From the physical nature of fillers, we assume that the different surface chemistry, and hence, the resultant incompatibility and poorer dispersibility are responsible for the inefficiency of CB/SiO₂ blends in the compounds to form strong filler network. The surface activity of the filler can be assessed through the surface energy γ ¹³

$$\gamma = \gamma^d + \gamma^p \tag{2}$$

in which γ^d and γ^p are the so-called dispersive and polar components, respectively.

According to Fowkes' model,¹⁶ the dispersive component of the adhesive energy, W_a^d , and the polar components of their surface free energy, W_a^p , can be presented as

$$W_a^d = 2(\gamma_{CB}^d \gamma_{Si}^d)^{1/2} \quad W_a^p = 2(\gamma_{CB}^p \gamma_{Si}^p)^{1/2} \tag{3}$$

The total adhesive energy, W_a , can be given by

$$W_a = W_a^d + W_a^p + W_a^h + W_a^{ab} \tag{4}$$

$$W_a = 2(\gamma_{CB}^d \gamma_{Si}^d)^{1/2} + 2(\gamma_{CB}^p \gamma_{Si}^p)^{1/2} + W_a^h + W_a^{ab} \tag{5}$$

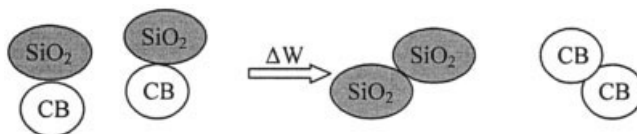
where W_a^h is the adhesive energy due to hydrogen bonding and W_a^{ab} the adhesive energy due to acid–base interactions.

When CB and SiO₂ agglomerate, a multitype of units will be formed in a dynamic process, as shown in Scheme 2. The change in potential energy, ΔW , can be written as

$$\Delta W = W_{CB-CB} + W_{SiO_2-SiO_2} - 2W_{CB-SiO_2} \tag{6}$$

If all other conditions (distance and size, etc.) are the same, W can be substituted by W_a

$$\begin{aligned} \Delta W = & 2[(\gamma_{CB}^d)^{1/2} - (\gamma_{SiO_2}^d)^{1/2}]^2 + 2[(\gamma_{CB}^p)^{1/2} - (\gamma_{SiO_2}^p)^{1/2}]^2 \\ & + 2[W_{CB}^h + W_{SiO_2}^h - 2W_{CB-SiO_2}^h] + 2[W_{CB}^{ab} \\ & + W_{SiO_2}^{ab} - 2W_{CB-SiO_2}^{ab}] \end{aligned} \tag{7}$$



Scheme 2 A schematic representation of change in energy associated with reagglomeration process for a filler blend system.

This equation suggests that when PMVS is charged with CB and SiO₂, the two fillers could form a randomly joint filler network, since CB and SiO₂ have totally different surface energy characteristics¹⁷ and ΔW is generally positive. This leads us into expectation that two filler network, SiO₂-SiO₂ and CB-CB network, and a mixture of two different filler agglomerates would most likely be formed. Consequently, the originally formed network (with only one type of filler) is partially deteriorated or retarded by other fillers blended together.

CONCLUSIONS

The incorporation of CB and SiO₂ filler-blends into PMVS result in a CB/SiO₂ ratio-dependent reducing *Payne effect* and a decreased Newtonian viscosity plateau in the low frequencies region. In combination with a simplified Fowke model, it is believed this phenomenon is resulted from the partially weakened filler interactions. Moreover, this interaction will lead to change of the filler network upon the addition of both CB and SiO₂ fillers.

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