Insights into the Payne Effect of Carbon Black Filled Styrene-butadiene Rubber Compounds

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Abstract As a widely used reinforcing filler of rubber, carbon black (CB) often enhances the nonlinear Payne effect and its mechanism still remains controversial. We adopt simultaneous measurement of rheological and electrical behaviors for styrene-butadiene rubber (SBR)/CB compounds and CB gel (CBG) during large deformation/recovery to investigate the contribution of conductive CB network evolution to the Payne effect of the compounds. In the highly filled compounds, the frequency dependence of their strain softening behavior is much more remarkable than that of their CB network breakdown during loading, while during unloading the unrecoverable filler network hardly affects the complete recovery of modulus, both revealing that their Payne effect should be dominated by the disentanglement of SBR matrix. Furthermore, the bound rubber adjacent to CB particles can accelerate the reconstruction of continuous CB network and improve the reversibility of Payne effect. This may provide new insights into the effect of filler network, bound rubber, and free rubber on the Payne effect of CB filled SBR compounds.

Keywords Payne effect; Styrene-butadiene rubber; Filler network

INTRODUCTION

The incorporation of nanoparticles (NPs) into rubbers can improve their mechanical performances and broaden their applications. Carbon black (CB) is widely used as a reinforcing filler in rubber industry on account of low price and its ability to form a hierarchical structure in a soft rubber matrix.[1] However, the mechanism of reinforcement and internal damping of rubber compounds is still controversial.[2] In general, NPs mostly exist in the form of aggregates in the rubber matrix, rather than monodisperse particles.[3] NP aggregates can adsorb and immobilize part of rubber molecular chains, resulting in the formation of bound rubber and interface layer, which further constitute the particle gel.[4] The mobility of rubber chains on the surface of NPs is limited and the glass transition of compounds widens at high temperature or low frequency, which affects the viscoelasticity of such materials.[5] The cluster-cluster aggregation (CCA) model[1] and percolation model[6] are often used to discuss the reinforcement effect of the particle network, but there is a huge contradiction between the theoretical prediction and experimental results, which can hardly explain the structure formation mechanism of the filled systems.

The Payne effect is an important topic in the investigation of rubber compounds viscoelasticity, featured by enormous decay of dynamic modulus with increasing strain amplitude (γ) beyond the linear viscoelastic region.[9,10] There are many theories proposed to interpret the Payne effect, which are usually ascribed to the agglomeration/deagglomeration of filler aggregates,[11] breakdown/reconstruction of filler network[12] or polymer-filler network,[11] chains desorption from NPs,[13] yielding of glassy layer surrounding NPs,[5] and disentanglement of chains in the adsorption layer.[14] The Payne effect is often neglected.[16] However, the assertions of softening as side effects are still in debate and so far not unambiguously identified due to the difficulties in directly visualizing the relevant microscopic structural evolutions during the deformation. Nowadays, the concepts of damages occurring in the filler structure and interfacial region are always all invoked to explain the strain softening, while the contribution of entangled or crosslinked rubbery matrix to the Payne effect of the compounds is often neglected.[16] However, the assertions of softening as side effects of the filler and viscoelastic rubbery matrix as a dispersing medium of the filler[19] can be hardly applied to the Payne effect of noncrystallizing gums[20] their vulcanizates[21,22] and slowly filled compounds.[23,24]

Due to the lack of direct visualization of the microstructural evolution during large deformation, researchers tried to in-
vestigate the effect of filler network on the Payne effect of rubber compounds with other indirect approaches. Gan et al. prepared the CB gel (CBG) by extracting free rubber from CB highly filled natural rubber (NR) compounds and systematically studied the rheological behavior of CBG. The Payne effect of CBG is reversible and independent of frequency (ω), while the bound rubber around CB can accelerate the modulus recovery during unloading. Simultaneous measurement of rheological and conductive properties could provide the real-time variation of viscoelastic and conductive behaviors induced by the evolution of microscopic condensed structure in different external fields (thermal field, shear field). In this work, we adopt this method to trace the synchronous evolution of volume resistance (R) and dynamic storage modulus (G) for CB filled styrene-butadiene rubber (SBR) compounds and CBG subjected to large oscillatory shear, and then pursue the breakdown/reconstruction of CB network and the modulus decay/recovery of the compounds and CBG. We attempt to clarify the effect of CB network on the Payne effect of the compounds and distinguish the respective contribution of CB network destruction/reconstruction, the bound rubber and free rubber disentanglement/entanglement to the modulus variation.

EXPERIMENTAL

Materials

Styrene-butadiene rubber (SBR, 1502; weight-averaged molecular weight \( M_w = 156 \text{ kg/mol, polydispersity } M_w/M_n = 3.31 \)) with a styrene content 18 wt% was obtained from Sinopec Qilu Co., Ltd., China. Carbon black (CB, Vxc-500; primary particle size ~30 nm, density ~1.8 g/cm\(^3\)) was produced by Cabot Co., Ltd., USA. Antioxidant \( N-(1,3\text{-dimethylbutyl})-N\text{-phenyl-p-phenylene}-\text{diamine} \) was obtained from Changzhou Xince Polym. Mater. Co., Ltd., China.

Sample Preparation

The CB/SBR compounds containing 1 phr (parts per hundred rubber) antioxidant were prepared by using a torque rheometer (X5S-300, Shanghai Kechuang Rubber & Plastic Machinery Co., Ltd., China) under 100 °C at a rotating speed of 40 r/min for 30 min. The compounds were compressed into sheets of 2 mm thickness on a press vulcanizer (XL-25, Huzhou Xinli Rubber Machinery Co., Ltd., China) at 100±5 °C under 14.5 MPa for 15 min. The un filled SBR was processed at the same conditions. Bulk carbon black gel (CBG) samples were obtained from compounds with high-loading fillers by solvent extraction of toluene and the specifications of specially designed extraction device were detailed in the literature. The disc-like CB/NR compounds were extracted from 800 mL of fresh toluene within 10 days at room temperature. The solvent was renewed twice every day. The extracted rubber in the solvent from the compounds was collected by rotary evaporation. After vacuum drying at room temperature for 48 h, the obtained bulk CBG was compression molded at 140 °C under 14.5 MPa for 40 min to ensure the integrity and flatness of CBG samples. The CBG samples obtained from highly filled compounds with different loadings have similar composition and microstructure and CBG in this work is extracted from SBR-0.224 (SBR-ϕ, ϕ is the volume fraction of CB).

Characterizations

The molecular weight information of SBR was obtained by gel permeation chromatography (GPC, Waters 2690, Waters Corp., USA) using tetrahydrofuran as mobile phase and polystyrene as standard calibration. The respective amount of SBR and CB in the compounds and CBG samples was determined by thermogravimetric analysis (TGA, Q1000, TA Instruments, USA). The samples were heated from 50 °C to 625 °C under a continuous nitrogen flow (50 mL/min). Glass transition temperature \( (T_g) \) and heat capacity of SBR in the compounds and CBG were measured by temperature-modulated differential scanning calorimetry (MDSC, Q100, TA Instruments, USA). Transmission electron microscopy (TEM, JEM-1230, JEOL, Japan) was used to investigate the dispersion of CB in the compounds under an acceleration voltage of 80 kV. The compounds were frozen and sliced to ultrathin slices about 100 nm in thickness.

A strain-controlled rheometer (ARES-G2, TA Instruments, USA) was adopted to investigate the linear and nonlinear dynamic rheological responses of the compounds and CBG samples at 140 °C. The volume resistance of the compounds was simultaneously detected by a digital picoammeter (Keithley 6487, Keithley Instruments Inc., USA) during rheological measurements. Here, the setup for simultaneous measurement of rheological and electrical behaviors was mentioned in our previous work and was not described in details. All the specimens were equilibrated for 5 min before performing frequency (ω) sweeps from 100 rad/s to 0.01 rad/s and strain (γ) sweeps from 0.01% to 100%. Strain amplitude (γ) sweeps from 0.01% to 100% and then from 100% to 0.01% at ω=1−50 rad/s were performed to study the nonlinear viscoelasticity.

RESULTS AND DISCUSSION

Composition and Structural Features

The microstructures of the compounds and CBG were studied by TEM. Fig. 1 shows the dispersion of CB in SBR/CB compounds with different loadings (ϕ=0.055−0.288) and CBG. The primary CB nanoparticles are assembled into small aggregates of tens of nanometers and well dispersed in the whole compounds and there are no large-scale agglomerates in the visual field. On the other hand, the extracted CBG sample presents a tightly packed granule morphology, and the residual bonding rubber connects the CB particles together to form a crowded filler network with uneven distribution. The micropores in the CBG sample correspond to the space occupied by the free rubber extracted out.

MDSC was used to study the ϕ dependence of the glass transition temperature \( (T_g) \) and the immobilized fraction \( \phi_{\text{imm}} \) for SBR/CB compounds and CBG, as shown in Fig. 2. \( T_g \) values of the compounds hardly change with the increase of CB loadings since CB only restrains the large scale motion of whole chains, while \( T_g \) of CBG is reduced by about 1 °C, which also occurred in NR/CB rubber system filled with CB and can be attributed to weak geometrical confinement effect arising from high CB volume fraction and the existence of a large.
number of microvoids.[25,29] Some SBR chains form a thin glassy layer surrounding CB nanoparticles and may lead to the decrease of the jump of reversing heat capacity ($\Delta C_p$) for SBR/CB compounds. Based on the sufficiently small $\Delta C_p$ value of CB, we can calculate the $\Delta C_p$ value of SBR fraction ($\Delta C_{p,SBR}$) in the samples by $\Delta C_{p,SBR} = \Delta C_p / (1 - x_{CB})$, where $x_{CB}$ is the mass fraction of CB in the samples. As the contribution of constrained rubber to the glass transition of the compounds is marginally small,[30] the immobilized fraction $\phi_{imm}$ or the glass layer encircling CB can be further determined by $\phi_{imm} = 1 - \Delta C_{p,SBR}/\Delta C_{p,SBR}^0$, in which $\Delta C_{p,SBR}^0$ is the $\Delta C_p$ value of neat SBR sample.[31] The $\phi_{imm}$ values increase with $\phi$, confirming the presence of glassy layer surrounding CB.

As a large amount of free rubber was extracted, the immobilized components were significantly higher in CBG. The interactions between the mobile SBR chains and CB masked by such glassy layer may result in no significant $T_g$ variation in the compounds or CBG.[32] Furthermore, the presence of a large number of free SBR chains may shield the calorimetric signals from the constrained and bridging chains.[30]

![Fig. 1](https://doi.org/10.1007/s10118-020-2462-2)

**Fig. 1** TEM micrographs of rubber compounds with different CB loadings: (a) SBR-0.055, (b) SBR-0.104, (c) SBR-0.148, (d) SBR-0.188, (e) SBR-0.224, (f) SBR-0.257, (g) SBR-0.288, (h) CBG-0.475.

**Linear Rheological Response**

In order to determine the percolation of CB in the filled compounds, small amplitude oscillatory frequency sweep measurements were carried out in the linear viscoelastic regime of the samples. Storage and loss moduli ($G'$ and $G''$) as a function of $\omega$ for SBR compounds containing CB at $\gamma=0.1\%$ and $T=140^\circ C$ are shown in Fig. 3(a). It is clearly seen that SBR exhibits nonterminal flow characteristics ($G' > G''$) in the whole investigated $\omega$ region. With the increase of $\phi$, the $\omega$ dependence of $G'$ in low $\omega$ region gradually weakens, and a typical "second platform" of filled system appears, indicating that the addition of CB hinders the long-time relaxation of SBR molecular chain. The appearance of such terminal platform is generally attributed to the decrease of the mobility of molecular chains adsorbed on the surface of fillers or the formation of the percolation network of particles through the rubber matrix.[33,34] With increasing $\phi$, the increment of $G'$ is greater than $G''$, indicating that the enhancement effect is more obvious than the dissipation effect with CB loading. The relative storage modulus $R'(\omega, \phi) = G'(\omega, \phi)/G''(\omega)$ for the compounds is usually used to discuss the reinforcement mechanism, where $G''(\omega)$ is the storage modulus of the matrix. The reinforcement is attributed to hydrodynamic effects at low $\phi$ and the formation of "jamming" or percolating network at high $\phi$. The critical concentration $\phi_c$ just defines the hydrodynamic to non-hydrodynamic transition.[35] On the basis of the time-concentration superposition (TCS) principle,[16,36] $R'(\omega, \phi)$ at different $\omega$s for SBR compounds can be normalized to a master curve as a function of $\phi/\phi_c$ as shown in Fig. 3(b). The applicability of normalization strategy indicates that the mechanism of hydrodynamic to non-hydrodynamic transition under different frequencies is consistent.

It is well known that for a homogenous polymer system, the time-temperature superposition (TTS) principle can be used to construct a master curve of viscoelastic property on a board frequency scale.[37] The applicability of TTS principle for the filled systems should be further explored. Fig. 4 shows the master curves of $G'$ and $G''$ for SBR compounds containing different loadings of CB and CBG by means of horizontal
The deviation of overlapping in low $\omega$ region for different SBR/CB compounds increases slightly with the increasing CB loading due to the inhibition of CB on the long-time relaxation of SBR molecular chains, while their master moduli curves in medium and high $\omega$ regions can be well obtained. As the $T_g$ values of SBR/CB compounds obtained from MDSC data are hardly influenced by the presence of CB, the horizontal shift factors $a$ of different SBR/CB compounds are mainly related with the polymer matrix and almost independent of CB loading, consistent with what has been observed in CB or silica filled elastomers.[38] However, the frequency scan curves of CBG at different temperatures cannot be superimposed in the whole frequency region only by horizontal shift and its frequency dependence of $G'$ and $G''$ is reduced due to
the sharp reduction of free rubber content in CBG. The failure of TTS principle for CBG may be attributed to the concealment of viscoelastic response of polymer matrix by a large amount of crowded CB particles.\textsuperscript{[26,28]} Hence, we can predict the linear viscoelastic response of SBR/CB compounds in high $\omega$ region by means of TTS principle.

**Payne Effect**

Beyond the linear regime, SBR and its compounds all exhibit typical nonlinear Payne effect, which is featured by remarkable modulus decay with increasing $\gamma$ and becomes increasingly marked with increasing $\phi$. The main origin of Payne effect for rubber compounds was often thought as the aggregation-disaggregation of fillers,\textsuperscript{[11,12]} destruction-reconstruction of rubber-filler interaction,\textsuperscript{[13]} and disentanglement chains at the interface/bulk phase.\textsuperscript{[14,17]} Here, simultaneous measurement of rheological and electrical behaviors of the highly filled compounds with conductive CB fillers can trace their structural evolution during large deformation, which should be helpful for elucidating the underlying mechanism of the Payne effect. Fig. 5 shows $G'$ and volume resistance ($R$) as a function of $\gamma$ for different SBR/CB compounds at different frequencies. With the extension of $\gamma$, $G'$ begins to decline after reaching a critical strain defined as $\gamma_{c}$, while $R$ rises significantly after a similar critical strain defined as $R_{c}$. With increasing CB loadings, the plateau $G'$ values of SBR/CB compounds in the linear regime increase as a result of reinforcement, while the plateau $R$ values before $R_{c}$ decrease from $10^{10}$ $\Omega$ to $10^{2}$ $\Omega$, indicating the presence of conductive filler network in the highly filled compounds.\textsuperscript{[26–28]} During large deformation loading, there may exist a competition between the breakdown and reconstruction of conductive CB network in SBR/CB compounds. As high viscosity of rubbery matrix restricts the movement of CB in the matrix at the investigated temperatures, the resistance variation in highly filled rubber systems is less obvious than that in filled thermoplastic systems.\textsuperscript{[26–28]} Here, at $\phi=0.188$ (40 phr CB), we can observe their resistance increment by about 1–2 orders of magnitude during loading. Hence, we can also trace the variation of volume resistance to explore the change of fillers network during large deformation. The plateau moduli increase with $\omega$ being consistent with dynamic viscoelasticity, while the plateau $R$ values hardly depend on $\omega$, suggesting no $\omega$ influence on the conductive CB network in the linear regime. With the increase of $\gamma$, the breakdown of conductive CB network in the rubber matrix may lead to the increment of $R$ value of the samples.\textsuperscript{[27]} Here, it should be noted that when $\phi=0.148$, the $R$ values of SBR/CB compounds are kept at about $10^3$ $\Omega$ and hardly vary with increasing $\gamma$, indicating the absence of conductive filler network in such compounds. In other words, the Payne effect of neat SBR and SBR compounds with $\phi=0.148$ should be irrelevant with the formation and breakdown of CB network. There exist some retracement points in the $R$ measurements under the strain sweep tests at low frequency, as the sample goes through a period from small strain to large strain in each strain testing cycle and the interval of resistance measurement is much shorter than that of strain sweep at low frequency.

Fig. 6 shows the $\omega$ dependence of the critical strains $\gamma_{c}$ and $R_{c}$ of $G'$ and $R$ for SBR/CB compounds. Here, we define the $\gamma_{c}$ value as the strain at which the modulus decreases by 5% relative to the platform modulus, while the $R_{c}$ value is also set as the strain at which $R$ rises by 5% relative to the platform resistance. SBR and its compounds all exhibit the decline of $\gamma_{c}$ with the increase of $\omega$ and the $\omega$ dependence of $\gamma_{c}$ for SBR compounds with different CB loadings is similar to that for neat SBR.\textsuperscript{[29]} Furthermore, the $\omega$ dependence and $\phi$ dependence of $R_{c}$ are both much weaker than those of $\gamma_{c}$ for SBR/CB compounds. In general, the variation of $R$ is just related with the aggregation-disaggregation of conductive
clusters during large deformation.[40] Namely, the influence of ω on the breakdown of conductive CB network is much smaller than that on their softening behaviors. Some models based on the aggregation-disaggregation of filler and the filler-matrix interaction might account for the ϕ-dependence of Payne effect,[31,12] while they could hardly explain the ω-dependence of critical strain. The abovementioned phenomena both suggest that the strain softening behavior for SBR/CB compounds might be dominated by the SBR matrix, rather than the filler network.

The contribution of filler to the nonlinear behavior can be further investigated by using the Fourier transformation of the stress (torque) and strain signals to separate the higher order harmonics.[41,42] In high order harmonics, the intensity of odd harmonics is higher than that of even harmonics, and the intensity decreases gradually. The third harmonic contributes the most of the higher harmonics to the nonlinear response, so the ratio of the third harmonic intensity i_3 to the first one i_1 is used to quantify the nonlinear degree. It can be found from Fig. 7(a) that i_3/i_1 for SBR increases exponentially with increasing ϕ, resulting from the orientation and stretch of the polymer chains,[41] while i_3/i_1 for SBR/CB compounds and CBG increases with increasing ϕ. Although different CB loadings cause different increasing rates of i_3/i_1 with the in-

Fig. 6 (a) γ_Gc and (b) γ_Rc as a function of ω at 100 °C for SBR/CB compounds with different CB loadings.

Fig. 7 (a) Relative third harmonic i_3/i_1 as a function of ϕ, (b) master curve of i_3/i_1 against γ at 10 rad/s, and (c) i_3/i_1 as a function of γ at different us for neat SBR, its compounds, and CBG. A_i is the strain amplification factor.
that the effect of frequency on the nonlinear degree of such systems can be nearly neglected. Such little \(\omega\) influence on the \(\gamma\) dependence of \(i_3/i_1\) is just consistent with that on the hydrodynamic to non-hydrodynamic transition (Fig. 3b), indicating that the nonlinearity of SBR and its compounds is much more sensitive to \(\gamma\) than \(\omega\).

**Recovery**

In order to further confirm the role of filler network during structural reconstruction, we performed cyclic strain amplitude sweep for neat SBR, its compounds, and CBG sample under different \(\omega\). Here, we synchronously traced their \(\gamma\) evolution of modulus and resistance during cyclic oscillation deformation with the maximum strain amplitude of 100% at 140 °C, as shown in Fig. 8. For neat SBR, no obvious recovery hysteresis can be observed under low and medium \(\omega\)s in the linear viscoelastic regime, while only at high \(\omega\) (50 rad/s) the \(G'\) hysteresis appears at \(\gamma>10\%\). The mechanical hysteresis of SBR is weaker than that of NR.[25,28] SBR-0.104 compound can exhibit the modulus recovery hysteresis at lower \(\omega\) (10 rad/s) owing to

| \(\omega\) (rad/s) | \(\gamma\) (%) |
|------------------|--------------|
| 1               | 0            |
| 5               | 1            |
| 10              | 2            |
| 50              | 3            |

| \(\omega\) (rad/s) | \(\gamma\) (%) |
|------------------|--------------|
| 1               | 0            |
| 5               | 1            |
| 10              | 2            |
| 50              | 3            |

**Fig. 8** \(G'\) and \(R\) as a function of \(\gamma\) for (a) neat SBR, (b) SBR-0.104, (c, d) SBR-0.224, and (e, f) CBG-0.475 during a loading (solid symbols)-unloading (hollow symbols) circle at 140 °C and different \(\omega\).
the amplification of micro-deformation for SBR in the filled system[15] and their $G'$ hysteresis increases with increasing $\omega$. For SBR-0.224 compound, there exist less obvious mechanical hysteresis and much remarkable resistance hysteresis. Furthermore, during unloading their moduli can almost return to the initial values completely under all $\omega$, while their resistance values largely deviate from the initial values by about two orders of magnitude, indicating that there is not enough time for the reconstruction of conductive CB network in the unloading process and the modulus recovery is almost unaffected by the reconstruction of filler network. Although CBG shows remarkable Payne effect at all investigated $\omega$, its modulus hysteresis at 1, 5, and 10 rad/s can be neglected owing to the absence of free rubber, while the resistance hysteresis can also be observed and recovered to the initial values in the unloading process. However, CBG exhibits marked $G'$ and resistance hysteresis at 50 rad/s in the whole investigated $\gamma$ regime and its resistance value still deviates remarkably from its initial value, indicating that the dramatic destruction of three-dimensional filler network structure in CBG only at high $\omega$ may result in difficult recovery of its mechanical modulus. Hence, it can be found that the modulus variation of Payne effect for SBR/CB compounds may be irrelevant to the destruction of filler network and their Payne effect may be recoverable, but the destruction of filler network is unrecoverable during a loading-unloading cycle.

We further explore the time-dependent behavior of Payne effect and modulus/resistance recovery by shearing neat SBR, compounds, and CBG stepwise to $\gamma=0.03\%$, 50%, and 0.03% at 140 °C and 1 rad/s. Here, we just trace the synchronous evolution of $R$ for SBR-0.188, SBR-0.224, SBR-0.254 compounds and CBG-0.474. Their time evolution of $G'$ and $R$ during three stages of shearing experiments is shown in Fig. 9. $G'$ and $R$ for all the samples almost remain constant at $\gamma=0.03\%$. Then subjected to shearing at $\gamma=50\%$, the samples exhibit a rapid $G'$ decay corresponding to a solid- to liquid-like transition[49] and the attenuation amplitudes of SBR-$\phi$ compounds increase with increasing $\phi$. Even $G'$ of CBG-0.474 decays with more than 3 orders of magnitude, much higher than those of SBR and its compounds. During stepwise shearing, the variation of $R$ for SBR-0.188 compound is very weak due to the absence of destruction and reconstruction of conductive CB network. $R$ values of SBR-0.224 and SBR-0.254 compounds show obvious time-dependent increments, while CBG exhibits an instantaneous $R$ increment, suggesting that the presence of free SBR may result in the delay of CB network damage. After being sheared back to $\gamma=0.03\%$, SBR/CB compounds show a partially instant and partially gradual recovery of $G'$, while their $R$ recovery processes are also gradual and much slower than their modulus recovery, indicating that the modulus recovery of SBR compounds should be little affected by the reconstruction of filler network. Furthermore, the recovery of $G'$ and $R$ for CBG exhibits notable instantaneity and is much more rapid than that of SBR compounds, revealing that the presence of bound rubber adjacent to CB particles can facilitate the reconstruction of CB network and improve the reversibility of Payne effect.[38,44]

In the CB filled compounds, the Payne effect is usually attributed to a variety of factors associated with filler, matrix, and the interface between filler and matrix. At $\phi>0.188$ (40 phr CB), simultaneous measurement of rheological and electrical behaviors during loading-unloading can clarify the effect of continuous filler network evolution on the viscoelastic response for the compounds. The $\omega$ dependence of the breakdown of CB filler network is much weaker than that of their strain softening behavior and the unrecoverable filler network hardly affects the complete recovery of modulus, both revealing that the Payne effect of highly filled compounds should be dominated by the disentanglement of free SBR matrix, rather than the breakdown of filler network.[29,38] Furthermore, the filler network surrounded by the bound SBR might improve the recovery of Payne effect[10,44]

CONCLUSIONS
Simultaneous measurement of rheological and electrical behaviors for the highly filled SBR/CB compounds and CBG during large deformation and recovery can clarify the contribution of filler network to the Payne effect of such compounds. Due to the presence of unrestricted free SBR, the linear viscoelastic response of filled compounds at high $\omega$ can be predicted by the TTS principle. The $\omega$ dependence of Payne effect is much

![Fig. 9](https://doi.org/10.1007/s10118-020-2462-2)
more obvious than that of CB network breakdown. During loading-unloading cyclic shear, the compounds show the ω-dependent modulus hysteresis and reversible modulus recovery, while their filler network cannot be recovered at all. In comparison, CBG exhibits ω-independent, nonhysteretic Payne effect and the CB network in CBG could be rapidly recovered. The Payne effect of the compounds mainly originates from the SBR matrix, rather than the breakdown and reconstruction of filler network. The bound rubber adjacent to CB might improve the recovery of Payne effect, while the free SBR matrix might delay the reconstruction of CB network. These results may provide some new evidences for clarifying the mechanism of the Payne effects for rubbery compounds.

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