

Payne Effect and Weak Overshoot in Rubber Nanocomposites

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 Electronic Supplementary Information

Abstract Payne effect and its associated weak overshoot are of importance for understanding and regulating the softening of rubber nanocomposites under large amplitude oscillations. Herein, Payne effect in diverse filled vulcanizates is investigated for generalizing the common characteristics. Master curves of strain amplitude dependent storage modulus are created with respect to microscopic strain amplitude of the matrix, revealing a matrix-dominated elastic nonlinearity being independent of type and dispersity of filler, crosslinking density and sol fraction of matrix and filler-rubber interfacial interactions. However, carbonaceous fillers with higher affinity to the rubber matrices yield lower strain amplification and higher overshoot behavior in comparison with siliceous silica. The investigation would be illuminating for preparing rubber nanocomposites with optimized reinforcement and softening performances.

Keywords Vulcanizate nanocomposites; Payne effect; Weak overshoot

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INTRODUCTION

Rubber nanocomposites widely used in industry^[1,2] demonstrate Payne effect,^[3–5] also named as Fletcher-Gent effect,^[6,7] under large amplitude oscillations, which depicting softening and dissipation behaviors is usually accompanied with weak overshoot of loss modulus (G'') depending on dispersity of the filler and its interactions with the rubber matrix.^[8–11] The Payne effect and its associated weak overshoot are usually attributed to the breakdown of filler network^[12–14] and the desorption of bounded chains from filler surface^[15–18] while recent studies show that the filler amplified viscoelastic deformation of the matrix is crucial.^[19]

The strain amplification effect is parameterized by strain amplification factor A_f , that is, the ratio of average strain of the matrix to the macroscopically imposed strain of the nanocomposites.^[20–24] It has been taken *a priori* as hydrodynamic factor^[25–27] for account for the reinforcement effect,^[28,29] storage modulus (G') at high frequencies (ω)^[30,31] or medium/high strain amplitudes (γ),^[24,32] and strain softening of the nanocomposites.^[33–42] It has been formulated based mainly on geometry considerations^[43–45] while its experimental values are highly dependent on topology^[46,47] and dispersity of the filler^[48–51] and its interaction with the rubber. Herein, we investigate the Payne effect in nitrile butadiene rubber (NBR), natural rubber (NR), styrene-butadiene rubber (SBR) and poly-

dimethylsiloxane (PDMS) nanocomposites filled with different fillers. The results show that the G' decay against γ is independent of the types of rubber and filler and therefore the interfacial interactions. On the other hand, A_f and the G'' overshoot of the nanocomposites with randomly crosslinked matrix differ with filler type. In comparison with silica, carbonaceous fillers give rise to lower A_f and higher relative intensity of G'' overshoot. By crosslinking PDMS with an end-linking method, however, the silica filled vulcanizates demonstrate very low relative intensity of G'' overshoot. The results would be instructive to understand the molecular mechanism of Payne effect and the influence of the filler.

EXPERIMENTAL

Materials

Nitrile butadiene rubber (NBR, trademark 4155; acrylonitrile content 41 wt%, and density 0.97 g/cm³) and natural rubber (NR, SVR3L grade; polyisoprene content 98%, and density 0.92 g/cm³) were obtained from Duokang, China. Styrene-butadiene rubber (SBR, 1502; styrene content 18 wt%, and density 0.92 g/cm³) was purchased from Sinopec Qilu Co., Ltd., China. Vinyl-terminated polydimethylsiloxane (PDMS) was obtained from Lijie Chem. Co., Ltd., China.

Carbon black (CB, trademark N330; primary particle size ~30 nm, and density 1.86 g/cm³) was obtained from Longxin Chem. Stock, China. Hydrophilic (A200, BET specific area of 200±25 m²/g and density of 2.20 g/cm³) and hydrophobic fumed silica products (R974, BET specific area of 170±20 m²/g and density of 2.20 g/cm³) were purchased from Evonik Degussa Co., Akron, OH, USA. Multi-walled carbon nanotubes

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(CNT, NC7000; average diameter of 9.5 nm, average length of 1.5 μm and density of 2.10 g/cm³) were from Nanocyl, Belgium. Oxide graphene (GO, lateral size of 5–10 μm , and thickness of 1.2 nm and density of 2.26 g/cm³) was home-made using a modified Hummer's method.

Triethoxysilane (C₆H₁₆O₃Si, TES) and *S*-(octanoyl)mercapto propyltriethoxysilane (C₁₇H₃₆O₄SSi, NXT) were obtained from Meryer (Shanghai) Chem. Techn. Co., Ltd., China and Gelest, Inc., USA, respectively. Bis[3-(triethoxysilyl)propyl]tetrasulfide (C₁₈H₄₂O₆S₄Si₂, Si69), tetrahydrofuran, pentaerythritol tetrakis(3-mercaptopropionate) (C₁₇H₂₈O₈S₄, PTT), 2,2-dimethoxy-phenylacetophenone (C₁₆H₁₆O₃, DPAP) and stearic acid were from Sinopharm Chem. Reagent Co., Ltd., China. Antioxidant 6PPD [*N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine], zinc oxide and accelerator CZ (*N*-cyclohexyl-2-benzothiazole sulfonamide) were obtained from Kunshan Anzhe Chem. Stock, China, Aladdin, China, and Tokyo Chem. Ind., Japan, respectively. Dicumyl peroxide (DCP) and sulfur were purchased from Aladdin, China and Zhejiang Yongjia Chem. Stock, China, separately.

Sample Preparation

Rubber (NR, NBR, SBR) compounds as per formula in Tables S1–S3 (in the electronic supplementary information, ESI) were prepared using an internal mixer (HOOK, Shanghai Kechuang Co., Ltd., China) at 100 °C for 35 min under 40 r/min and were cured in press vulcanizer (XL-25, Huzhou Xinli Rubber Machinery Co., Ltd., China) at 140 °C and 14.5 MPa for 30 min. Randomly crosslinked PDMS nanocomposites were prepared by mixing PDMS, DCP and silica (R974) in tetrahydrofuran at 150 r/min for 60 min and after volatilizing solvent, curing in the press vulcanizer at 140 °C and 14.5 MPa for 45 min. In comparison, nanocomposites based on end-linking PDMS chains were prepared *via* photoinitiated thiol-ene crosslinking reaction. In tetrahydrofuran, PDMS, crosslinker PTT, initiator DPAP and filler R974 were stirred in a three-necked flask at 150 r/min for 60 min under nitrogen flow. The dispersions transferred into transparent glass models were exposed to UV light irradiation (Uvhand 100, Hönle; 365 nm, 5 mW/cm²) at 365 nm wavelength for 60 min. The gel-like materials were dried at room temperature in air for 72 h. Apparent crosslinking density (ν_c) and sol fraction of rubber (w_{sol}) were measured by equilibrium swelling in toluene or dichloromethane at room temperature (Figs. S1–S4 in ESI). For the nanocomposites containing carbonaceous filler, w_{sol} is less than 10% and ν_c increases with increasing filler volume fraction (ϕ) (Figs. S1 and S2 in ESI), which may be mainly assigned to the adsorption of rubber chains onto the aggregates,^[52] yielding slightly elevated glass transition temperature (Fig. S5 in ESI) and trapped entanglements^[53,54] acting as loose, indestructible junctions^[55] in the chemically crosslinked network.^[56] For the NBR nanocomposites containing hydrophilic silica (A200), ν_c decreases and w_{sol} increases with increasing filler volume fraction (ϕ) (Fig. S3 in ESI) because silica aggregates partially absorb the curatives incorporated and the free radicals generated by vulcanization.^[57] By introducing silanes or by using hydrophobic silica (R974), ν_c increases and w_{sol} decreases at given ϕ . Silica has poor affinity with hydrophobic rubbers and it may slightly depress glass transition temperature of the mobile phase (Figs. S6 in ESI).

Measurements

The vulcanizates were cut into disks of 25 mm in diameter for rheological test. The strain amplitude (γ) sweeps were measured by a strain-controlled rheometer (ARES-G2, TA Instruments, USA) at angular frequency (ω) 1 rad/s and temperature 25 °C. Glass transition temperature of NBR in the vulcanizates was measured using dynamic mechanical analyzer (Q800, TA, USA) with a cantilever mode at a heating rate of 3 °C/min, frequency of 10 Hz and oscillation amplitude of 30 μm (Figs. S5 and S6 in ESI). The dispersity of filler in the vulcanizates was observed by transmission electron microscopy (JEM-1200EX, JEOL, Japan) at an accelerating voltage of 300 kV (Figs. S7 and S8 in ESI).

RESULTS

Fig. 1 displays nonlinear rheological responses of CB filled NBR, NR and SBR vulcanizates. Above a critical amplitude (γ_c), storage modulus (G') decreases with increasing strain amplitudes (γ). Simultaneously, loss modulus (G'') overshoots near γ_c . The weak overshoot, a feature of vulcanizates,^[34–37,58,59] involves in intermolecular friction^[58] of network chains with an extremely broad distribution^[54] and the redistribution of deformation and orientation between subchains of different lengths.^[60] With increasing ϕ , the G' and G'' values in the linear viscoelastic region (G'_0 and G''_0) increase and γ_c decreases due to strain amplification effect^[29,61–64] and the overshoot weakens due to the formation of bridging chains and entrapped entanglements.^[54] For all the vulcanizates, G'/G'_0 could be normalized by shifting the data along the γ axis by a factor of A_f . The master curve reflects the nonlinear elasticity of finitely extensible rubber network.^[4,34,37,40,58,61,65–67] The superposition beyond the linear viscoelastic region fails for G''/G''_0 due to the occurrence of overshooting.

Fig. 2 shows Payne effect and its normalized plots for GO and CNT filled NR vulcanizates. Both fillers exhibiting some degree of agglomeration (Fig. S8 in ESI) improve G'_0 slightly at ϕ up to 0.041 but at considerably low contents they cause a slight reduction in G''_0 . Fig. 3 shows the results of hydrophilic silica (A200) and hydrophobic silica (R974) filled NBR vulcanizates. In the linear region, A200 exhibits a lower reinforcement effect than R974, which is ascribed to the poor dispersity of A200 (Fig. S7 in ESI) in the matrix with the lower ν_c and higher w_{sol} (Fig. S3 in ESI). Fig. 4 displays the Payne effect and its normalized plots for A200 filled NBR vulcanizates containing different silanes. The introduction of silanes somewhat improves the reinforcement efficiency due to the improvement of A200 dispersity and the generation of finely dispersed silica aggregates (Fig. S7 in ESI). Due to the crosslinking nature of the matrix, the Payne effect is less sensitive to temperature (Fig. S9 in ESI).

Fig. 5 shows Payne effect and its normalized plots for silica filled PDMS vulcanizates cured by end-linking and random crosslinking methods. In comparison with the ones with the randomly crosslinked matrix, those with end-linking matrix exhibit a slower G' decay and weaker G'' overshoot in the nonlinear region, being consistent with the previous results.^[68]

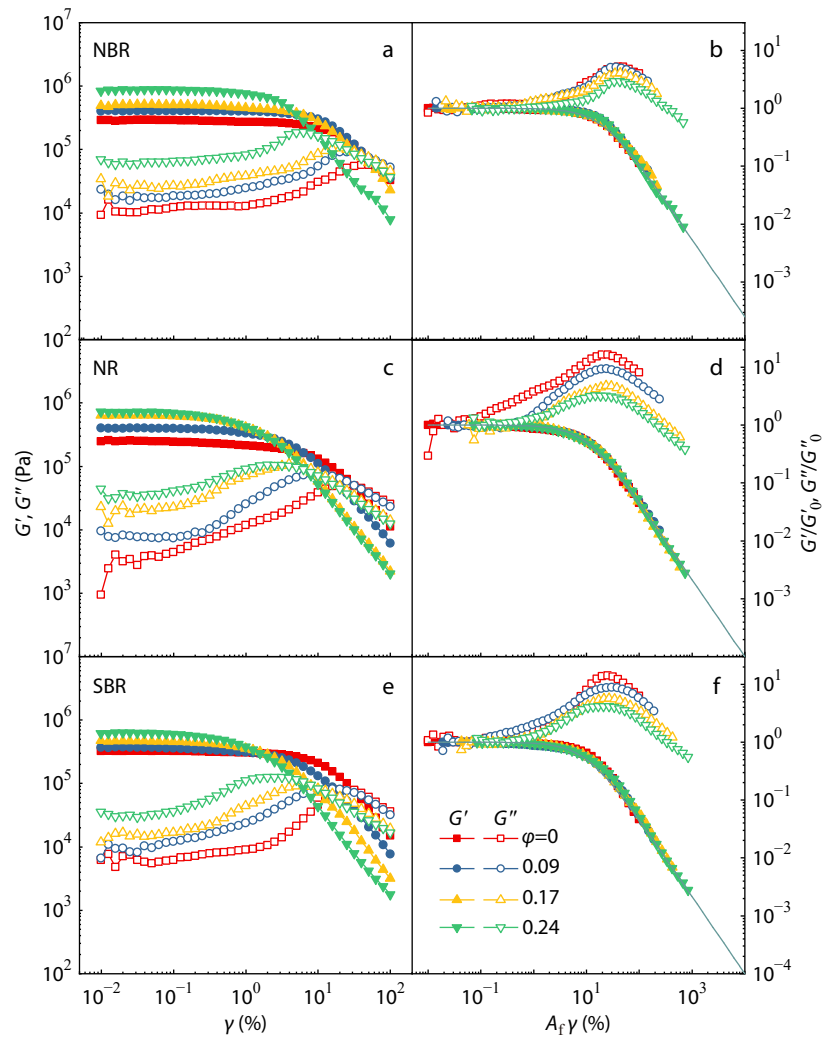


Fig. 1 G' (solid symbols, a, c and e) and G'' (hollow symbols, a, c and e) as a function of γ and their normalized plots (b, d and f) at 373 K for CB filled NBR (a and b), NR (c and d) and SBR vulcanizates (e and f). Solid curves in (b), (d) and (f) are drawn following empirical expression of Rouse dynamics.

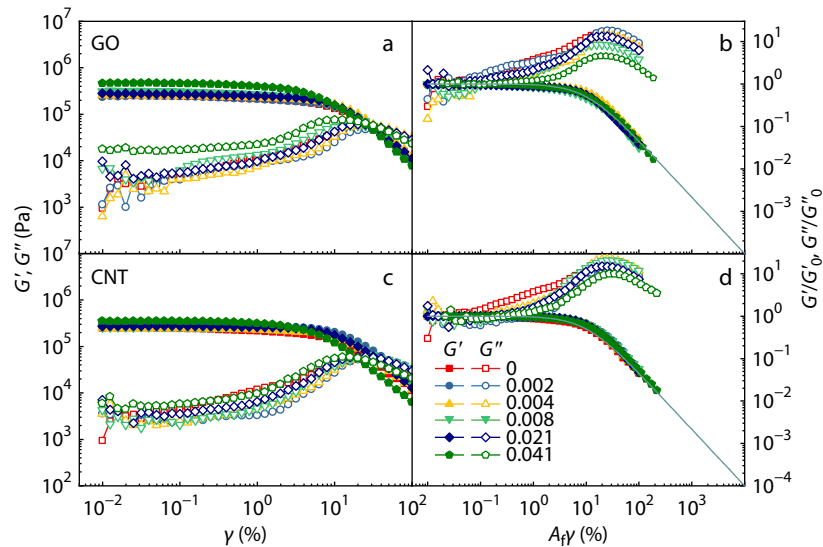


Fig. 2 G' (solid symbols, a and c) and G'' (hollow symbols in a and c) as a function of γ and their normalized plots (b and d) at 373 K for GO (a and b) or CNT (c and d) filled NR vulcanizates. Solid curves in (b) and (d) are drawn following empirical expression of Rouse dynamics.

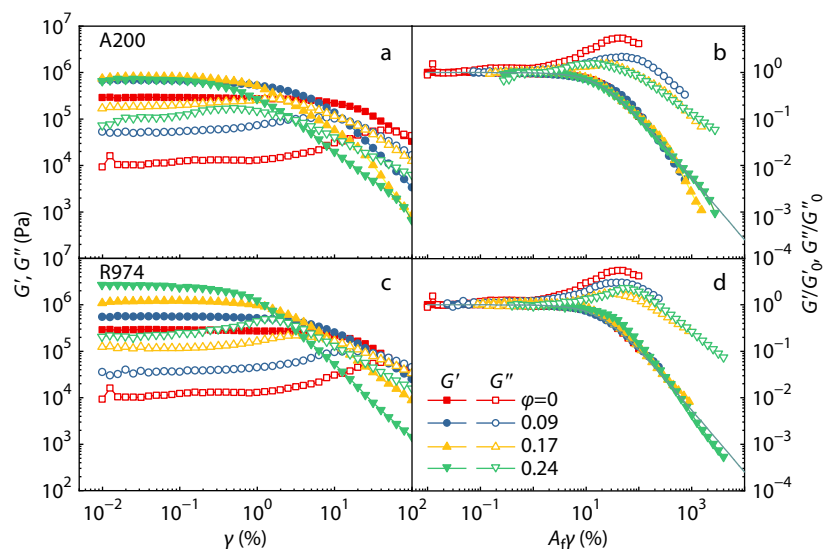


Fig. 3 G' (solid symbols, a and c) and G'' (hollow symbols, a and c) as a function of γ and their normalized plots (b and d) at 373 K for A200 (a and b) or R974 (c and d) filled NBR vulcanizates. Solid curves in (b) and (d) are drawn following empirical expression of Rouse dynamics.

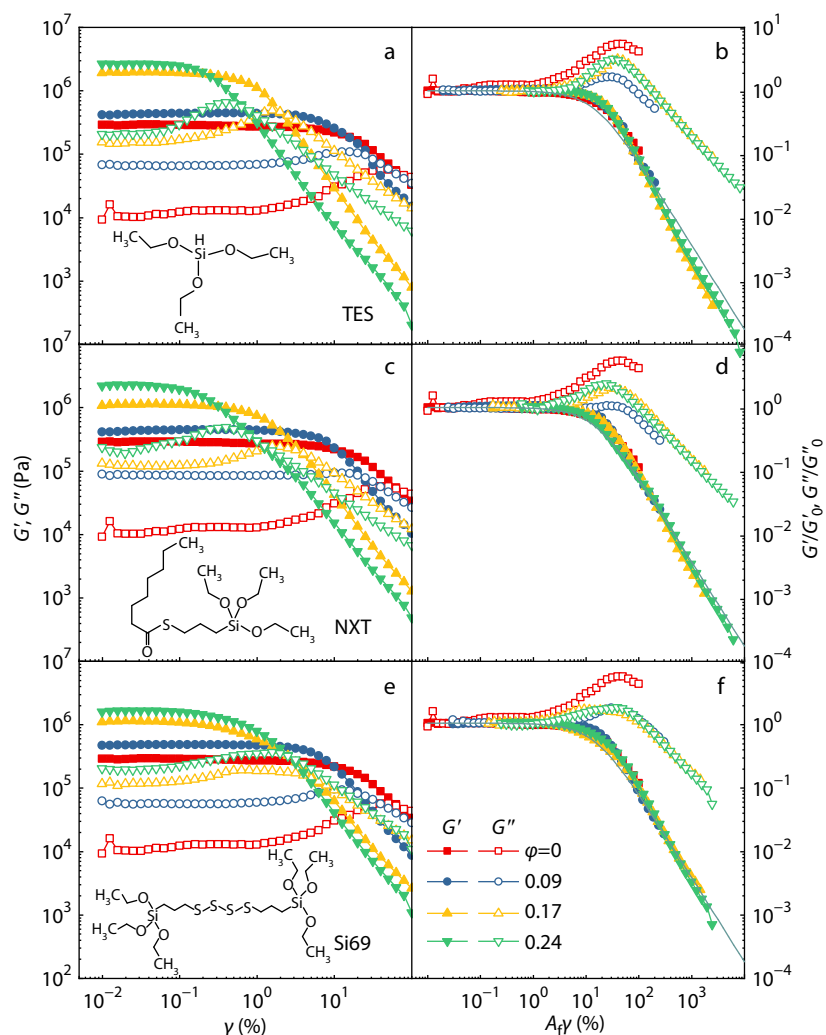


Fig. 4 G' (solid symbols, a, c and e) and G'' (hollow symbols, a, c and e) as a function of γ and their normalized plots (b, d and f) at 373 K for A200/NBR vulcanizates containing TES (a and b), NXT (c and d) or Si69 (e and f). Solid curves in (b), (d) and (f) are drawn following empirical expression of Rouse dynamics.

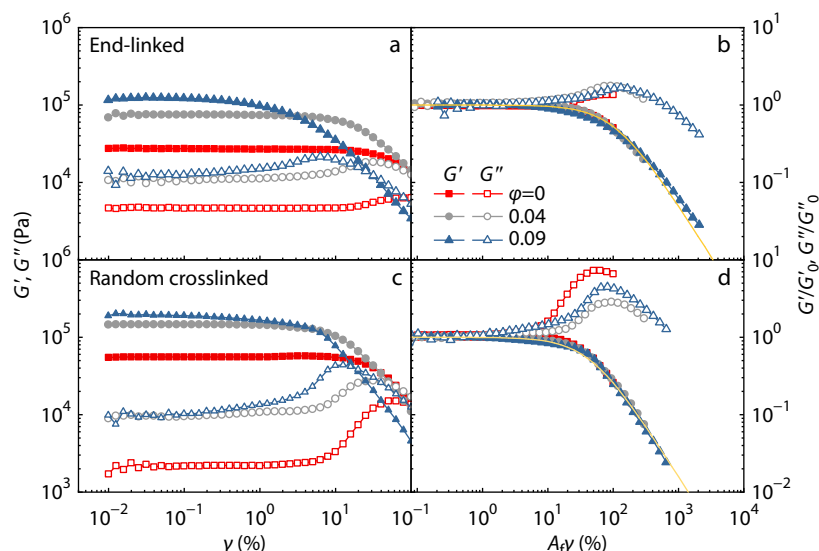


Fig. 5 G' (solid symbols in a and c) and G'' (hollow symbols in a and c) as a function of γ and their normalized plots (b and d) at 373 K for silica filled PDMS vulcanizates cured by end-linking (a and b) and random crosslinking methods (c and d). Solid curves in (b) and (d) are drawn according to empirical expression of Rouse dynamics.

DISCUSSION

Oscillating deformation affects the motion of chains^[69] in the defective crosslinking network by activating the convective constraint release and reducing the tension of subchains.^[66,70] The Rouse model taking into account of finite chain extension predicts a $-2/3$ power law^[71–73] for steady viscosity at high shear rates, or a $G' \sim \gamma^{-4/3}$ scaling law^[74] in the low- ω nonlinear oscillating regime. This scaling law is included into an empirical relation $G'/G'_0 = 1/[1 + (A_f \gamma / \gamma_{cm})^{4/3}]$ ^[75–77] that approximates G'/G'_0 of the vulcanizates of diverse compositions (Figs. 1–5). Here, γ_{cm} is a critical strain amplitude for the Payne effect of the gum vulcanizates. It means that the nanocomposites composed by diverse rubbers and fillers demonstrate a general elasticity nonlinearity that is dominated by Rouse retraction of the matrix and is insensitive to the crosslinking density and filler-rubber interactions.

The appearance of Payne effect, depicted G'_0 , γ_c and G'' overshoot, is undoubtedly dependent on filler dispersity, rubber crosslinking density and filler-rubber interaction. Fig. 6 shows strain amplification factor, A_f , as a function of ϕ and relative intensity of overshoot (G''_{max}/G''_0) as a function of G''_0 for clarifying the common characteristics in different nanocomposites. Despite that the data are somewhat dispersed due to the multiple influencing factors, general trends are observed. In comparison with the vulcanizates filled with silica, those filled with carbonaceous fillers demonstrate lower A_f values at given ϕ and higher G''_{max}/G''_0 values at $G''_0 < 0.1$ MPa, which might be related to the higher affinity of carbonaceous fillers and rubber matrices. In the silica filled vulcanizates, A_f does not sensitively reflect the silica dispersity mediated by silica hydrophobicity and silanes (Fig. S7 in ESI) and G''_{max}/G''_0 exhibits a minimum at $G''_0 = 0.1$ MPa, indicating a transition from rubber to filler dominated overshoot behavior with increasing ϕ . The filler-dominated overshoot at high ϕ is related to friction among particles of the silica agglomerates. However, the silica filled end-linking PDMS exhibits G''_{max}/G''_0

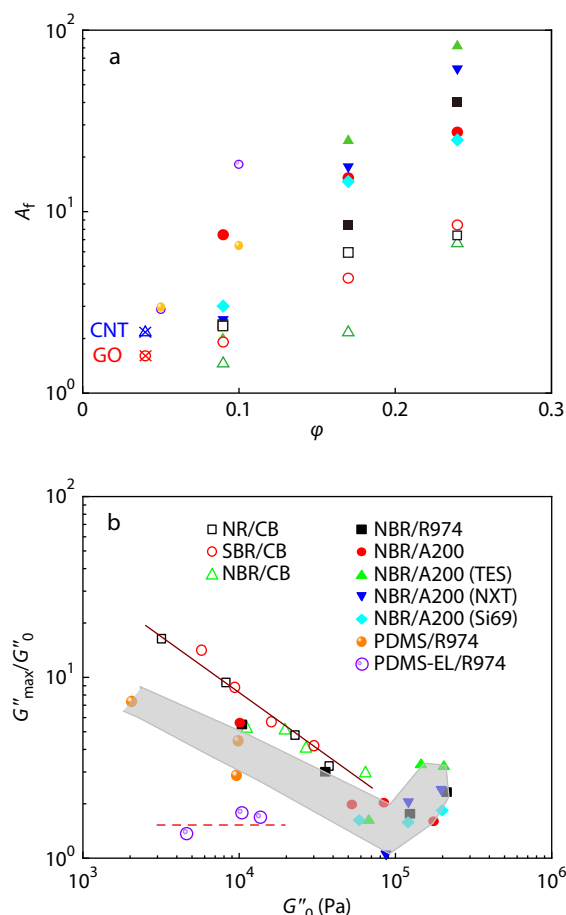


Fig. 6 A_f as a function of ϕ (a) and relative intensity of G'' overshoot (G''_{max}/G''_0) as a function of G''_0 for the vulcanizates. The solid and dotted lines and the shadowed region are for guide of the eyes.

as low as 0.15, which could be related to the low network defects.^[68]

CONCLUSIONS

The vulcanizate nanocomposites of diverse compositions demonstrate Payne effect and weak overshoot behaviors being dominated by the viscoelastic deformation of the rubber matrix with defective crosslinking network. The filler amplifies the microscopic strain of the matrix, which is more significant for the silicious than the carbonaceous fillers. While both the silicious and carbonaceous fillers tend to lower intensities of the weak overshoot, the serious agglomeration of silica may cause interparticle friction to intensify the overshoot at high filler loadings. On the other hand, the interaction between silica and rubber based on covalent bonding from silanization tends to intensify the strain amplification effect and filler-rubber interfacial friction.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-021-2643-7>.

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