

Understanding the Reinforcement and Dissipation of Natural Rubber Compounds Filled with Hybrid Filler Composed of Carbon Black and Silica*

Yi-hu Song^{a**}, Ling-bin Zeng^b and Qiang Zheng^a

^a Ministry of Education Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Key Laboratory of Adsorption and Separation Materials & Technologies of Zhejiang Province, Zhejiang University, Hangzhou 310027, China

^b Shanghai Aerospace System Engineering Institute, Shanghai 201110, China

Abstract The performance of reinforced rubber compounds depends on the filler composition while the reinforcement and dissipation mechanisms still remain unclear. Herein linear and nonlinear dynamic rheological responses of carbon black/silica hybrid filler filling nature rubber compounds are investigated. The rheological contributions of dynamically retarded bulk phase and filler network are revealed to be crucial at high and low frequencies, respectively, and the bulk phase is shown to be of vital importance for the occurrence of nonlinear Payne effect at mediate frequencies. A framework for simultaneously solving reinforcement and dissipation varying with filler composition and content is suggested, providing a new perspective in understanding the filling effect for manufacturing high-performance rubber materials.

Keywords Filling; Reinforcement; Dissipation; Rubber compounds; Time-concentration superpositioning principle

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INTRODUCTION

Nanoparticles significantly reinforce rubbers because they form filler network and influence the properties of the matrix close to the filler surfaces^[1–4]. In the reinforced rubbers, there are both immobilized chains surrounding nanoparticles and bridging chains interconnecting adjacent nanoparticles^[5, 6], resulting in a coherent bulky filler gel (BFG) network that interpenetrates through the rubbery entanglement network^[7]. The compounds at small strain amplitude γ exhibit a linear rheological response featured by large increases in complex modulus $G^*(\omega, \phi)$ and appearance of modulus plateau at low frequency ω with increasing filler volume fraction ϕ ^[1–4]. Also introduced by filling is the striking nonlinear strain softening or Payne effect^[8–10] featured by an enormous drop of $G^*(\gamma, \phi)$ with increasing γ during dynamic shearing. In prevailing theories, the reinforcement is usually assigned to hydrodynamic effect at low ϕ and filler structuring effect at moderately high ϕ ^[1–4] and popular interpretations of the nonlinear Payne effect resort to dynamic deagglomeration of filler agglomerates and

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** Corresponding author: Yi-hu Song (宋义虎), E-mail: s_yh0411@zju.edu.cn

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breakup of filler network or polymer-filler network mediated by desorption of chains and variation of bound rubber (BdR) fraction in the close vicinity of filler aggregates^[11].

Understanding the filling effect is the key for developing reduced energy-loss compounds for automobile tires and other applications^[12, 13]. Carbon black (CB) and silica are commonly used for reinforcing the rubbers. Their combination in proper ratios could modify compounding behavior, weaken the Payne effect^[14], and improve mechanical properties of vulcanizates with regard to each single filler^[15], which becomes a common strategy in fabricating “green” tread rubbers^[16] with balanced performance. The advances are promising in industrial applications while the influence of filler composition on the reinforcement and dissipation remains yet unclear. Herein linear and nonlinear rheological behaviors of CB and precipitated silica filled natural rubber (NR) compounds are thoroughly investigated. By varying the CB to silica ratio (CSR) at totally 50 phr (parts per hundred rubber) filler, the compound’s rheology is adjusted and the influences of CSR on the viscoelastic contributions of the filler and the bulk polymer phases are discussed. Dynamically retarded bulk phase is revealed to be of significance to the reinforcement and dissipation of the compounds at high ω while molecular disentanglement in this phase is proved to be important for initiating the nonlinear Payne effect. Influences of CSR on rheological contributions of the filler phase in the low ω and high γ regimes are addressed based on creating master curves of both linear and nonlinear rheological responses. It is revealed for the first time that, though the degrees of dynamics retardation and strain amplification of the bulk phase vary with CSR, both the reinforcement and dissipation of the compounds as a function of ω and ϕ could be normalized onto time-concentration superpositioning master curves, which helps to shed light on the longstanding controversies about the reinforcement mechanisms.

EXPERIMENTAL

Materials

Natural rubber (NR, SVR3L grade; density $0.92 \text{ g}\cdot\text{cm}^{-3}$, weight-average molecular weight $1120 \text{ kg}\cdot\text{mol}^{-1}$, polyisoprene content 98%, polydispersity index 3.57) was purchased from Shanghai Duokang Ind. Co., Ltd., China. Carbon black (CB, N330; ash content less than 0.5%, cetyltrimethyl ammonium bromide adsorption $(82 \pm 9) \text{ m}^2\cdot\text{g}^{-1}$, dibutyl phthalate adsorption $1.0 \text{ cm}^3\cdot\text{g}^{-1}$, nitrogen surface area $(78 \pm 7) \text{ m}^2\cdot\text{g}^{-1}$, iodine adsorption $(82 \pm 5) \text{ g}\cdot\text{kg}^{-1}$) and precipitated silica (ZQ356; silica content 97.3%, cetyltrimethyl ammonium bromide adsorption $184 \text{ m}^2\cdot\text{g}^{-1}$, dibutyl phthalate adsorption $5.5 \text{ cm}^3\cdot\text{g}^{-1}$) were, respectively, purchased from Tianjin Lihua Chem. Ind. Co., Ltd., and Zhuzhou Xinglong Chem. Ind. Co., Ltd., China. Antioxidant *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine was obtained from Changzhou Xince Polym. Mater. Co., Ltd., China. Silane bis(γ -triethoxysilylpropyl)tetrasulfide (commonly known as Si69 in rubber industry) was obtained from Hangzhou Jessica Chem. Co., Ltd., China. All the materials were used as received.

Sample Preparation

Silica (100 g) and silane (8 g) were premixed in a high-speed mixer (Wuhan Yiyang Plastic Machinery Co., Ltd., China) for 10 min. NR compounds containing 1.6 phr antioxidant and 50 phr filler were prepared using a two-roll open mill (XK-160, Zhanjiang Rubber & Plastic Machinery Co., Ltd., China) according to a standard procedure elaborated in ASTM-D3192. The compounds after storage for more than 1 day were thermally treated under vacuum at $140 \text{ }^\circ\text{C}$ for 30 min for promoting the formation and stabilization of BdR^[17]. They were compressed into sheets of 2 mm in thickness on a press vulcanizer (XL-25, Huzhou Xinli Rubber Machinery Co., Ltd., China) at $(100 \pm 5) \text{ }^\circ\text{C}$ under 10 MPa for 10 min. The sheets were cut into discs of 25 mm in diameter.

Characterization of the Compounds

A strain-controlled rheometer (ARES-G2, TA Instrument, USA) was used to measure dynamic rheological responses of the compounds at $100 \text{ }^\circ\text{C}$ using a plate-plate geometry with a serrated surface texture to prevent slipping. All the specimens were equilibrated for 5 min before performing frequency (ω) sweeps from $100 \text{ rad}\cdot\text{s}^{-1}$ to $0.0158 \text{ rad}\cdot\text{s}^{-1}$ at a dynamic strain amplitude $\gamma = 10^{-3}$. Strain sweeps from $\gamma = 10^{-4}$ to 1 were

performed at $\omega = 1 \text{ rad}\cdot\text{s}^{-1}$. Differential scanning calorimetry (DSC) was conducted on a differential scanning calorimeter (TA Q100, TA Instruments, US). Samples (5–10 mg) sealed in aluminum pans were quenched down to -80°C at a rate of $10 \text{ K}\cdot\text{min}^{-1}$ and were equilibrated for 3 min. DSC curves were recorded during the second run of heating at the same rate. Scanning electron microscopy (SEM, S-4800, Hitachi, Japan) was adopted to investigate the filler dispersion. The samples were cryogenically fractured in liquid nitrogen and the fractured surfaces were coated with gold-palladium using a Denton Desk-1 vacuum sputter coater (Denton Vacuum, LLC, USA).

RESULTS AND DISCUSSION

Figure 1 shows SEM images of fractured surfaces of the compounds containing 50 phr filler of different CSRs. It is seen that both fillers are well dispersed in the matrix. The fractured surface of the CB compound is coarse while that of the silica compound is rather smooth, indicating that the filler-polymer interaction in the former is higher than that in the latter. According to extraction experiment, the compounds contain 45%–50% free rubber and 17%–21% BdR in weight; the BdR content increases very slightly with increasing CSR.

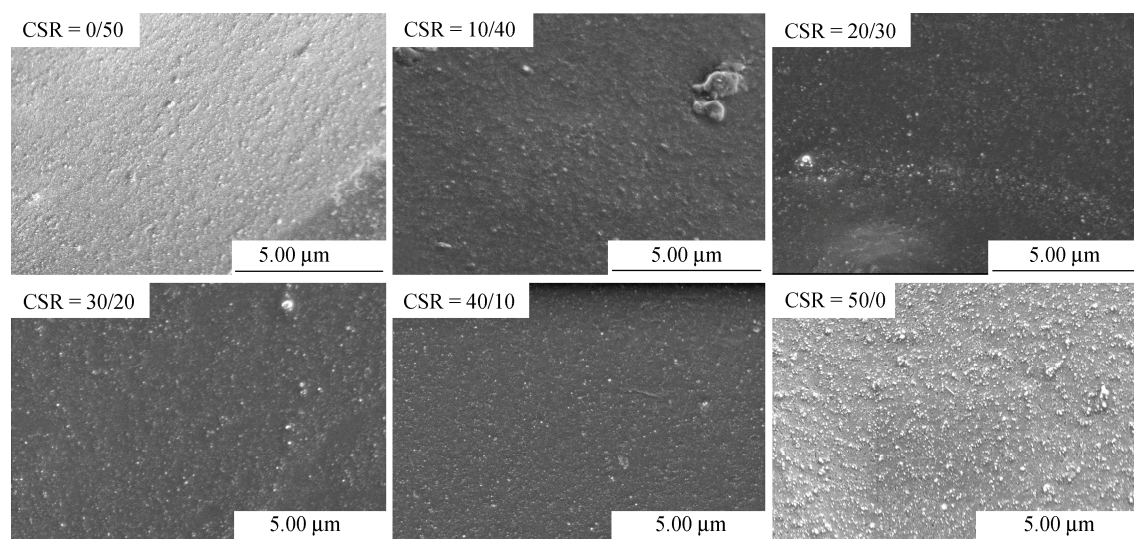


Fig. 1 SEM images of the compounds with different CSRs indicated

Figure 2 shows DSC curves of the compounds. The heat flow is normalized with respect to rubber mass. Glass transition temperature (T_g) and half-width of temperature range of glass transition (ΔT_g) are determined as $(-66.9 \pm 0.2)^\circ\text{C}$ and $(2.9 \pm 0.2)^\circ\text{C}$, respectively, both being the same as those of pure NR. The constant T_g being independent of filling is ascribed to the structural heterogeneity where the filler only influences relaxation of chains localized in a nanosized range near the surface of nanoparticles^[18].

Figure 3(a) shows storage modulus (G') and loss modulus (G'') and Fig. 3(b) shows loss tangent ($\tan\delta$) as a function of ω for the compounds dynamically sheared at $\gamma = 10^{-3}$. At low frequencies, NR exhibits the typical terminal flow characterized by scaling laws of $G'_m(\omega) \sim \omega^2$ and $G''_m(\omega) \sim \omega^1$ accompanying with a sustained decay of $\tan\delta_m$ as a function of ω . Here the subscript m indicates the matrix. Filling improves $G'(\omega, \phi)$ and $G''(\omega, \phi)$ and such improvements are large in the low ω region^[19]. All the compounds are solid-like ($G' > G''$, and $\tan\delta < 1$ in the test ω range) with appearance of a broad $\tan\delta$ peak, which has been assigned to the flow restrictions induced by filler structures^[20] and incomplete relaxation of the percolated filler network^[21] accompanying with slowed down dynamics^[22] of chains adsorbed on filler surface^[23]. Both $G'(\omega, \phi)$ and $G''(\omega, \phi)$ vary with CSR and they are the minimum at CSR = 30/20 where the BdR content is the highest (22%). With increasing CSR, $\tan\delta$ increases and its peak shifts somewhat towards low frequencies. Figure 3(c) shows variations of $G'(\omega, \phi)$ and

$G''(\omega, \varphi)$ at $0.01582 \text{ rad}\cdot\text{s}^{-1}$ as a function of CSR, which clearly demonstrates the influence of CSR on both the reinforcement and dissipation with the appearance of minimum modulus values at CSR = 30/20.

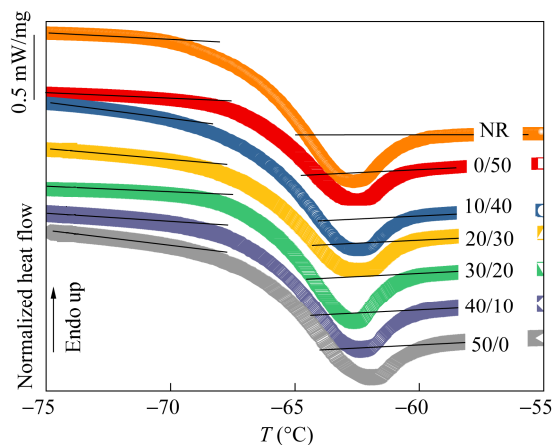


Fig. 2 Heat flow normalized by mass of polymer in the compounds

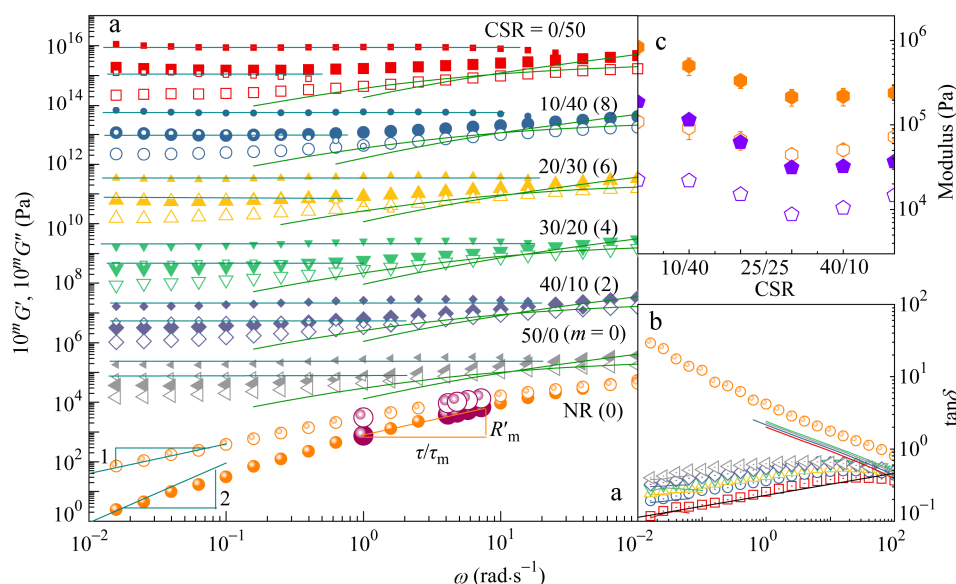


Fig. 3 Linear rheology for the compounds: (a) G' (large solid symbols), G'' (large hollow symbols) and (b) $\tan \delta$ as a function of ω , and (c) G' (solid pentagon) and G'' (hollow pentagon) of the compounds at $0.01582 \text{ rad}\cdot\text{s}^{-1}$ as well as $G'_f(\varphi)$ (solid hexagon) and $G''_f(\varphi)$ (hollow hexagon) of the filler phase as a function of CSR

In (a), the data are vertically shifted by a factor of 10^m for clear display; the curves on the high ω side show the rheological contribution of the bulk phase; the small symbols with horizontal lines on the low ω side represent the rheological contribution of the filler phase; the large circles marked on the data of NR show variations of rheology due to dynamics retardation from relaxation time τ_m of pure NR to $\tau(\varphi)$ of the bulk phase, yielding a relative change of storage modulus R'_m . In (b), the curves on the high and low ω sides are drawn according to $G''_m(\omega\tau/\tau_m)/G'_m(\omega\tau/\tau_m)$ arising from the bulk phase and $G''_f(\varphi)/G'_f(\varphi)$ from the filler phase, respectively.

Accompanied by filler structuring and chain adsorption, filling always retards global chain diffusion^[24]. The linear rheology of the compounds could be approximated by a modified two phase (MTP) model, $G^*(\omega, \varphi) = (1 - \varphi)A_f(\varphi)G_m^*(\omega\tau/\tau_m) + \varphi G_f^*(\omega, \varphi)$ ^[25]. This model has been verified in CB, fullerene, multi-walled carbon nanotubes and graphite nanoplatelets filled polystyrene of different molecular weights^[25, 26]. In this model, $A_f(\varphi)$

is a strain amplification factor, defined as the ratio of microscopic strain of interstitial fluid in the bulk phase to macroscopic strain imposed on the compounds. τ_m is terminal relaxation time of pure NR and $\alpha(\varphi)$ is that of the bulk phase in the compounds. $G_m^*(\omega\tau/\tau_m)$ and $G_f^*(\omega, \varphi)$ are complex moduli of the bulk and filler phases, respectively. $G_f^*(\omega, \varphi)$ has been approximated phenomenologically based on different considerations^[2, 4, 27–41]. To account for $G_f^*(\omega, \varphi)$ properly, the structure and rheology of BFGs extracted from the compounds are investigated, as shown in the supporting information (SI). The BFGs contain 33%–39% (in weight) BdR whose T_g is about 1.3–2.6 °C higher than that of pure NR, indicating a slightly restrained α relaxation. BFGs contain 41%–47% (in volume) filler whose aggregates interconnect each other to form an integrated network^[42]; there are no distinct large-scale agglomerates. There are abundant defects-like micropores and ravines of ~100 nm in size, corresponding to the space of extracted rubber; these defects could not be eliminated even after compression moulding BFGs at elevated temperatures^[43]. The linear rheology of BFGs measured at $\gamma = 3 \times 10^{-4}$ is nearly independent of ω up to 10 rad·s⁻¹, reflecting a viscoelastic pseudo-network consisting of nanoparticles interconnected by chain bridges^[44]. G' , G'' and $\tan\delta$ of the BFGs at $\omega < 10$ rad·s⁻¹ are located in the ranges of 24–139 kPa, 1.6–5.2 kPa and 0.03–0.08, respectively, and they are nearly independent of CSR and BdR content. The $\tan\delta$ values are considerably lower than those of the compounds, suggesting that the BdR and filler network are beneficial for reducing mechanical hysteresis^[45]. On the contrary, the high $\tan\delta$ values of the compounds arise largely from the free (extractable) rubber fractions rather than BFGs and their BdR fractions. According to the measured linear rheology of BFGs, an ω -independent complex modulus $[G_f'(\varphi) + iG_f''(\varphi)]$ ^[27, 30, 37] is used for approximating $G_f^*(\omega, \varphi)$ for the highly-filled compounds.

The MTP model is used to fit the measured $G^*(\omega, \varphi)$ data in Fig. 3(a). The terminal relaxation time τ_m for the pure matrix is simply identified as reciprocal of $G_m'(\omega)$ - $G_m''(\omega)$ crossover frequency. The fitting by a trial-and-error method allows estimation of the φ -dependent parameters $[A_f(\varphi)$, $\alpha(\varphi)$, $G_f'(\varphi)$ for $G'(\omega, \varphi)$, and $A_f(\varphi)$, $\alpha(\varphi)$, $G_f''(\varphi)$ for $G''(\omega, \varphi)$]. The best fitting values of $G_f'(\varphi)$ and $G_f''(\varphi)$ are shown in Fig. 3(c). They are the minimum at CSR = 30/20 and are significantly higher than G' and G'' values of BFGs measured in the linearity regime. The higher $G_f'(\varphi)$ and $G_f''(\varphi)$ values could be assigned on the one hand to the cooperation between the free and bound rubber fractions in the compounds and on the other hand to the existence of defects in BFGs^[43]. In the compounds, the viscoelastic filler structure involves interconnected filler aggregates, adsorption layer and entrapped chains^[46]. Especially, the filler structuring *via* nanoparticles colliding and sticking is mediated by bridging chains partly adsorbed on the filler surface and partly entangled with neighboring chains^[47]. Thus the entanglement between the free (extractable) chains in the bulk phase and the bridging chains in the filler network is important for retarding the chain diffusion and reinforcing the compounds^[48]. As shown in Fig. 3(a), the linear rheology of the compounds is mainly related to the strain amplification effect in the dynamically retarded bulk phase, expressed as $(1 - \varphi)A_f(\varphi)G_m^*(\omega\tau/\tau_m)$. As shown in Fig. 3(b), $\tan\delta$ of the compounds in the low and high ω limits could be approximated by $G_f''(\varphi)/G_f'(\varphi)$ and $G_m''(\omega\tau/\tau_m)/G_m'(\omega\tau/\tau_m)$, respectively, revealing that the filler and bulk phases play the dominative roles in these two zones.

The $A_f(\varphi)$ and $\alpha(\varphi)$ values are used to normalize the linear rheology in the polymer-determined high ω zone, *i.e.*, the hydrodynamic regime^[49], as shown in Fig. 4. The normalizations of reduced storage and loss moduli, $G_f'(\omega, \varphi) = G'(\omega, \varphi)/[(1 - \varphi)A_f(\varphi)]$ and $G_f''(\omega, \varphi) = G''(\omega, \varphi)/[(1 - \varphi)A_f(\varphi)]$, and $\tan\delta$ against reduced frequency, $\omega\alpha(\varphi)$, approve the MPT model. The retarded dynamics of the bulk phase are able to account for reinforcement and dissipation simultaneously in the hydrodynamic regime for the compounds of varying CSR. The dynamics retardation becomes weaker with increasing CSR and $\alpha(\varphi)/\tau_m$ reaches the minimum at CSR = 30/20 (inset in Fig. 4a) where $G'(\omega, \varphi)$ and $G''(\omega, \varphi)$ of the compounds at 0.01582 rad·s⁻¹ as well as $G_f'(\varphi)$ and $G_f''(\varphi)$ of the filler phase all are the minimum (Fig. 3c). On the other hand, $A_f(\varphi)$ seems to be independent of CSR and its mean lies in (3.31 ± 0.28) .

Relative storage modulus, $R'(\omega, \varphi) = G'(\omega, \varphi)/G_m'(\omega)$, is usually used to discuss the reinforcement mechanism^[2–4, 36]. No theory could account for the φ -dependence of relative loss modulus, $R''(\omega, \varphi) = G''(\omega, \varphi)/G_m''(\omega)$, which is normally smaller than $R'(\omega, \varphi)$ at given ω and φ . Figure 5(a) shows reduced relative moduli $R_f'(\omega, \varphi) = R'(\omega, \varphi)/[(1 - \varphi)A_f(\varphi)]$ and $R_f''(\omega, \varphi) = R''(\omega, \varphi)/[(1 - \varphi)A_f(\varphi)]$, which are horizontally shifted

by a factor of a_ω (inset in Fig. 5a) to collapse onto the data of silica compound (CSR = 0/50). Creation of the $R'_r(\omega, \varphi)$ and $R''_r(\omega, \varphi)$ masters suggests that the filling-induced variations of reinforcement and dissipation follow the same mechanism despite the variation of CSR. The a_ω factor reflects the relative change of overall relaxation time of the compounds, which differs from the relative change of terminal relaxation time of the bulk phase characterized by $\tau(\varphi)/\tau_m$ (inset in Fig. 4a).

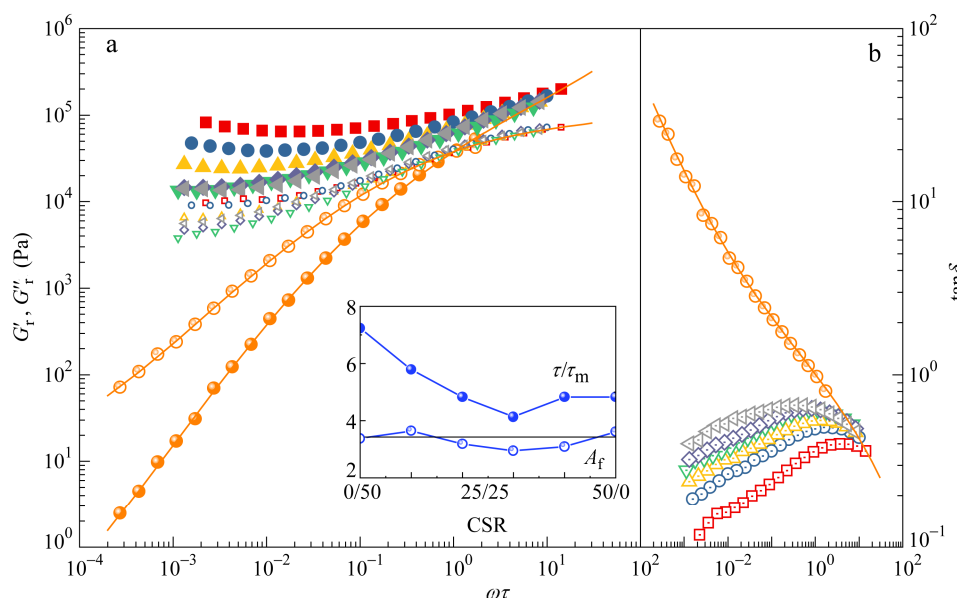


Fig. 4 Normalized linear rheology for the compounds: (a) G'_r (large solid symbols) and G''_r (small hollow symbols) and (b) $\tan\delta$ as a function of $\omega\tau$

Inset in (a) shows A_f and τ/τ_m for the compounds of varying CSR. The curves are drawn according to least-square fit to the data of compounds collapsed onto that of NR. The legends in (a) and (b) are the same as those in Fig. 1.

The reinforcement has been discussed within the frameworks of hydrodynamic effect at low φ ^[3] and “jamming” or percolating phenomena at φ above a threshold φ_c ^[2–4, 36]. However, the existing theories could not well describe the experimental discrepancies even taking into the filler aggregation and chain adsorption into consideration. For reinforcement at $\varphi > \varphi_c$ that is frequently described by scaling law $R'(\omega, \varphi) \sim \varphi^x$ at arbitrarily designated frequencies, the experimental values (0.2–7.2) of x exponent are significantly different from those (2.0–5.0) predicted by cluster-cluster aggregation or fractal yielding models^[4]. Many attempts seeking microscopic influence factors meet frustrations because the experimental x values are sensitive to ω where the linear rheology is analyzed^[4, 6]. Considering that the polymer and filler play crucial roles in the hydrodynamic and non-hydrodynamic regimes^[1–4, 36], respectively, an attempt is made to create $R'(\omega, \varphi)$ and $R''(\omega, \varphi)$ master curves by normalizing φ with an ω -dependent critical concentration $\varphi_c(\omega)$ defining the transition from the linearity to scaling regimes. The created master curves are shown in Fig. 5(b) for the compounds of varying CSR. Also shown are data from the silica compounds (CSR = 0/50) of varying φ (0.04–0.17). The master curves are surprisingly identical for the compounds containing 50 phr hybrid filler of varying CSR and for those containing silica of varying φ , disclosing a profound time-concentration superpositioning principle that is able to account for $R'(\omega, \varphi)$ and $R''(\omega, \varphi)$ against φ and ω simultaneously. It means that the filling-induced rheological variation at high ω is somewhat equal to that at low φ . The created master curves at $\varphi > \varphi_c(\omega)$ could be described by $R'(\omega, \varphi) \sim \varphi^{4.2}$, and $R''(\omega, \varphi) \sim \varphi^{2.2}$, respectively; the former follows the prediction for nonfluctuating fractal objects^[50] while the latter is never clarified and is simply ignored in traditional theories. The normalization strategy is of significance for clarifying the longstanding disagreements in reinforcement studies^[1–4, 36]. Note that $\varphi_c(\omega)$ differs from the traditional percolation threshold (φ_c) that is assumed to be an ω -insensitive geometrical

parameter but is never accurately predicted^[1–4]. The parameter $\varphi_c(\omega)$ here depicts a unique linearity-to-scaling transition, or hydrodynamic-to-jamming regime transition. Though microstructure of the filler phase may vary with CSR, the reinforcement and dissipation could be well accounted for by introducing the parameter $\varphi_c(\omega)$ that increases with $a_\omega\omega$ coincidentally for the different compounds, as shown in the inset of Fig. 5(b). It is suggested that this parameter is determinately related to the overall relaxation of the compounds mediated by cooperation motions of both the bulk and filler phases. According to the created time-concentration superpositioning principle, “frequency” is very important for the reinforcement and dissipation of the compounds. The apparent solid like rheology of the highly filled compounds involves two competitive sources, *i.e.*, the polymer-dominated hydrodynamic effect that prevails at high ω and low φ and the filler-dominated scaling behavior that is significant at low ω and high φ . The scaling behavior usually observed in the low ω terminal region works only when the bulk phase relaxes fully. It becomes clear that the relaxation of the bulk phase is vital for a full understanding of the compound’s viscoelasticity.

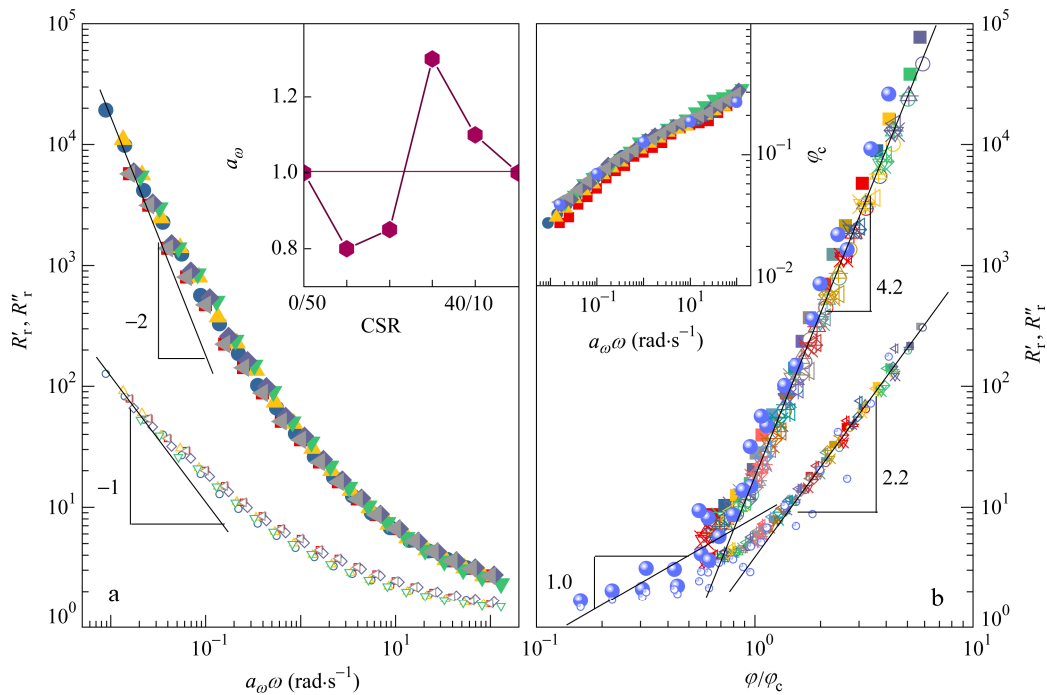


Fig. 5 Normalized linear rheology for the compounds: (a) R'_r (large solid symbols) and R''_r (small hollow symbols) as a function of $a_\omega\omega$, and (b) R'_r (large symbols) and R''_r (small symbols) as a function of φ/φ_c . Inset in (a) shows a_ω for the compounds of varying CSR and that in (b) shows φ_c as a function of $a_\omega\omega$. The sphere symbols represent data from the silica compounds with $\varphi = 0.04, 0.08, 0.11, 0.14$, and 0.17 , and $\omega = 100, 10, 1, 0.1$ and $0.01582 \text{ rad}\cdot\text{s}^{-1}$, respectively. The legends in (a), (b) and inset in (b) are the same as those in Fig. 1.

With increasing γ beyond the linearity regime, the Payne effect takes place, as shown in Figs. 6(a) and 6(b) for the compounds of varying CSR. $G'(\gamma)$, $G''(\gamma)$ and $\tan\delta$ remain constant at γ below an onset strain of nonlinearity (γ_c). At high γ amplitudes, $G'(\gamma)$ and $G''(\gamma)$ decrease and $\tan\delta$ increases with γ . Note that γ_c of the compounds is more than 100 times of that ($\sim 2 \times 10^{-4}$) of BFGs. Furthermore, the compounds exhibit a rapid modulus recovery within 30 s after a predetermined γ amplitude (0.1) located in the nonlinearity regime is switched to a small γ amplitude (2×10^{-3}) in the linearity regime, as shown in the supporting information. In comparison, the modulus recovery of BFGs is not complete after γ is switched from 1×10^{-2} to $\sim 2 \times 10^{-4}$ and repeated γ switching between these two small γ amplitudes lowers the degree of modulus recovery due to accumulated destruction of the filler structure. Clearly, the presence of free rubber fractions improves the

straining resistance and facilitates the structural recovery. Because the breakdown of filler aggregates generated by direct filler-filler interaction cannot conceivably be a function of time^[51], the modulus recovery must be mediated by the bulk phase that plays a dominant role in the reinforcement and nonlinear response.

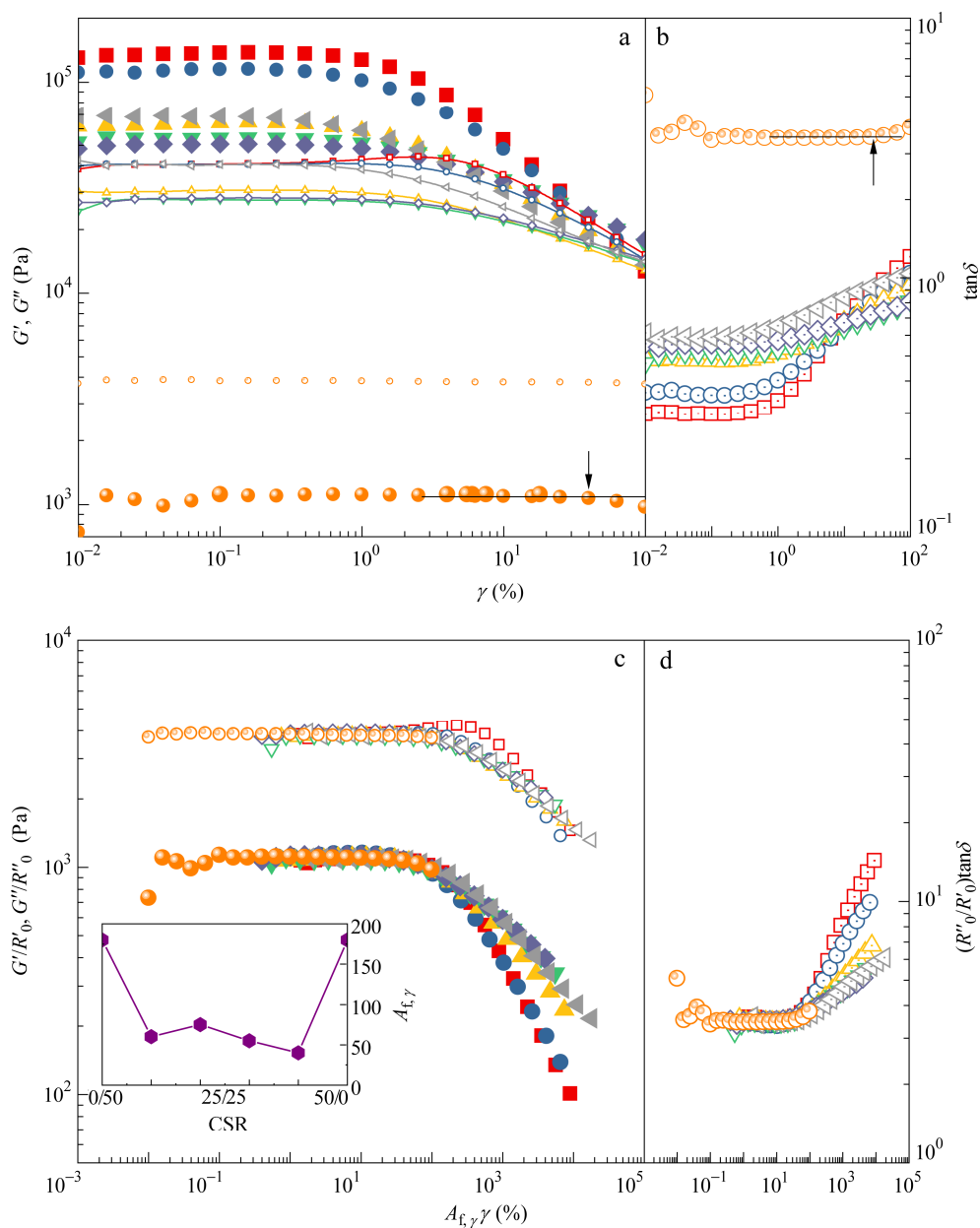


Fig. 6 Nonlinear rheology and its master curves for the compounds at 1 rad·s⁻¹: (a) G' (large solid symbols) and G'' (small hollow symbols) and (b) $\tan \delta$ as a function of γ ; (c) G'/R_0 (solid symbols) and G''/R_0 (hollow symbols) and (d) $(R''_0/R_0)\tan \delta$ as a function of $A_{t,\gamma}$. Inset in (c) shows $A_{t,\gamma}$ for the compounds of varying CSR. The legends in (a), (b), (c) and (d) are the same as those in Fig. 1.

γ of the compounds is much smaller than that (~ 0.3) of pure NR, which should be related to the strain amplification effect that causes the nonlinearity to occur^[52]. The silica compound (CSR = 0/50) exhibits a very weak $G''(\gamma)$ overshoot accompanying with the onset of Payne effect, which may arise from fluctuation,

migration, and rearrangement of silica aggregates^[53, 54]. The coexistence of CB and silica inhibits the $G''(\gamma)$ overshoot, improves γ_c and lessens the $G'(\gamma)$ and $G''(\gamma)$ decays in the nonlinearity regime. It is suggested that the gradual replacement of silica by CB would reduce the filler-filler interactions and simultaneously improve the filler-polymer interactions, thus improving the filler dispersity and decreasing the Payne effect. The nonlinear rheological curves could be superposed onto those of pure NR by horizontal shift by a factor of $A_{f,\gamma}(\varphi)$ followed by a vertical shift by factors of $1/R'_0$ and $1/R''_0$ for $G'(\gamma)$ and $G''(\gamma)$, respectively, as shown in Fig. 6(c). Here, $A_{f,\gamma}(\varphi)$ reflects the ratio of microscopic to macroscopic strain for the onset of Payne effect, which is considerably higher than $A_f(\varphi)$ determined from the linear rheology (inset in Fig. 4a). R'_0 and R''_0 are relative storage and loss moduli determined at small γ amplitudes in Fig. 6(a). The data superposition before the onset of Payne effect is confirmed by plotting $(R''_0/R'_0)\tan\delta$ as a function of $A_{f,\gamma}(\varphi)\gamma$, as shown in Fig. 6(d). According to created master curves, the nonlinear rheological data from the different compounds collapse rigorously before the divergence in the nonlinearity regime, which suggests that the Payne effect is initiated by mechanisms lying in the macromolecular events^[1, 52, 55–58]. For the ω -sweep rheology tested at $\gamma = 10^{-3}$, the critical microscopic strain $A_{f,\gamma}(\varphi)\gamma_c$ of the bulk phase being responsible for the onset of Payne effect in the compounds is in the range of 0.04–0.18, being smaller than γ_c of NR. It means that the ω -sweep reported in Fig. 3 really represents the linear rheology of the compounds. It is for long assumed that the Payne effect involves the breakdown of filler aggregates^[10] or network^[59] *via* release of entrapped entanglement, desorption of adsorbed chains, and reduction of number of chains bridging adjacent nanoparticles^[60]. Considering that it also occurs in entangled polymers and low-filling compounds^[61], the Payne effect should be largely related to over orientation and disentanglement of finitely extensible chains in the bulk phase^[62]. Nevertheless, the rheology in the nonlinearity regime is influenced by the filler phase depending on CSR, as shown in Figs. 6(c) and 6(d). The increment of $\tan\delta$ becomes gradually gentle with increasing CSR and it is finally identical for the compounds with CSRs of 30/20, 40/10 and 50/0. In comparison with silica, the coexistence of CB and silica tends to improve the network stability (decelerates the $\tan\delta$ increment) in the nonlinearity regime.

CONCLUSIONS

Both linear and nonlinear rheological responses are dependent on CSR of the compounds. The bulk rubber phase with retarded dynamics is crucial for both reinforcement and dissipation of the compounds in the hydrodynamic regime while the filler network characterized by nearly ω -independent $G'_f(\varphi)$ and $G''_f(\varphi)$ becomes overwhelmingly dominant at low ω . Despite of microstructural differences in the filler phase, the linear rheology could be well accounted for by introducing an ω -dependent linearity-to-scaling transition concentration $\varphi_c(\omega)$. The disclosed time-concentration superpositioning principle works for the compounds containing 50 phr hybrid filler of varying CSR and for those containing silica of varying φ , indicating that the filling-induced reinforcement and dissipation involve two competitive sources, *i.e.*, the polymer-dominated hydrodynamic effect prevailing at high ω and low φ and the filler-dominated scaling behavior being significant at low ω and high φ . On the other hand, the Payne effect is rooted in the macromolecular disentanglement that is strikingly accelerated *via* strain amplification effect induced by the filler phase. The strain amplification factor $A_{f,\gamma}(\varphi)$ for initiating molecular disentanglement is considerably higher than that being responsible for the hydrodynamic effect of the dynamically retarded bulk phase in the linearity regime.

REFERENCES

- 1 Song, Y., Du, M., Yang, H. and Zheng, Q., *Acta Polymerica Sinica* (in Chinese), 2013, (9): 1115
- 2 Song, Y. and Zheng, Q., *J. Rheol.*, 2015, 59: 155
- 3 Song, Y. and Zheng, Q., *Crit. Rev. Solid. State.*, 2016, 41: 318
- 4 Song, Y. and Zheng, Q., *Prog. Mater. Sci.*, 2016, 84: 1

- 5 Kosinski, L.E. and Caruthers, J.M., *Rheol. Acta*, 1986, 25: 153
- 6 Zhu, Z.Y., Thompson, T., Wang, S.Q., von Meerwall, E.D. and Halasa, A., *Macromolecules*, 2005, 38: 8816
- 7 Wolff, S., Wang, M.J. and Tan, E.H., *Rubber Chem. Technol.*, 1993, 66: 163
- 8 Payne, A.R., *J. Appl. Polym. Sci.*, 1964, 8: 2661
- 9 Payne, A.R., *J. Appl. Polym. Sci.*, 1963, 7: 873
- 10 Payne, A.R., *J. Appl. Polym. Sci.*, 1960, 3: 127
- 11 Meera, A.P., Said, S., Grohens, Y. and Thomas, S., *J. Phys. Chem. C*, 2009, 113(42): 17997
- 12 Robertson, C.G., *Rubber Chem. Technol.*, 2015, 88: 463
- 13 Tsai, Y.T., Chiou, J.Y., Liao, C.Y., Chen, P.Y., Tung, S.H. and Lin, J.J., *Compos. Sci. Technol.*, 2016, 132: 9
- 14 Rattanasom, N., Saowapark, T. and Deeprasertkul, C., *Polym. Test.*, 2007, 26(3): 369
- 15 Bokobza, L., *Rubber Chem. Technol.*, 2013, 86: 423
- 16 Zhang, P., Morris, M. and Doshi, D., *Rubber Chem. Technol.*, 2016, 89: 79
- 17 Dannenberg, E.M., *Rubber Chem. Technol.*, 1975, 48: 410
- 18 Kraus, G. and Gruver, J. T., *J. Polym. Sci., Part A2: Polym. Phys.*, 1970, 8: 571
- 19 Shabbir, A., Goldansaz, H., Hassager, O., van Ruymbeke, E. and Alvarez, N.J., *Macromolecules*, 2015, 48: 5988
- 20 Scherzer, S.L., Pavlova, E., Esper, J.D. and Sary, Z., *Compos. Sci. Technol.*, 2015, 119: 138
- 21 Dalmas, F. and Leroy, E., *Macromolecules*, 2011, 44: 8093
- 22 Zhang, Y., Zuo, M., Liu, T., Song, Y. and Zheng, Q., *Compos. Sci. Technol.*, 2016, 123: 39
- 23 Hyun, Y.H., Lim, S.T., Choi, H.J. and Jhon, M.S., *Macromolecules*, 2001, 34: 8084
- 24 Lin, C.C., Gam, S., Meth, J.S., Clarke, N., Winey, K.I. and Composto, R.J., *Macromolecules*, 2013, 46: 4502
- 25 Song, Y., Tan, Y. and Zheng, Q., *Polymer*, 2017, 112: 35
- 26 Song, Y., Zeng, L. and Zheng, Q., *Compos. Sci. Technol.*, 2017, 147: 39
- 27 Carrot, C., Majesté, J.C., Olalla, B. and Fulchiron, R., *Rheol. Acta*, 2010, 49: 513
- 28 Chen, Q., Gong, S., Moll, J., Zhao, D., Kumar, S.K. and Colby, R.H., *ACS Macro Lett.*, 2015: 398
- 29 Choong, G.Y.H., de Focatiis, D.S.A. and Hassell, D.G., *Rheol. Acta*, 2013, 52: 801
- 30 Majesté, J.C., Carrot, C., Olalla, B. and Fulchiron, R., *Macromol. Theory Simul.*, 2012, 21: 113
- 31 Song, Y., Sun, J. and Zheng, Q., *Acta Polymerica Sinica (in Chinese)*, 2009, (8): 729
- 32 Song, Y. and Zheng, Q., *Polymer*, 2010, 51: 3262
- 33 Song, Y. and Zheng, Q., *Polymer*, 2011, 52: 593
- 34 Song, Y. and Zheng, Q., *Polymer*, 2011, 52: 6173
- 35 Song, Y. and Zheng, Q., *Acta Polymerica Sinica (in Chinese)*, 2012, (12): 1383
- 36 Song, Y. and Zheng, Q., *Polymer Bulletin (in Chinese)*, 2013, 15(9): 22
- 37 Song, Y., Zheng, Q. and Cao, Q., *J. Rheol.*, 2009, 53: 1379
- 38 Wang, J., Wu, D.F., Li, X. and Zhang, M., *Polym. Eng. Sci.*, 2013, 53: 2541
- 39 Wu, D., Wang, J., Zhang, M. and Zhou, W., *Ind. Eng. Chem. Res.*, 2012, 51: 6705
- 40 Yu, W., Wang, J. and You, W., *Polymer*, 2016, 98: 190
- 41 Tan, Y., Yin, X., Chen, M., Song, Y. and Zheng, Q., *J. Rheol.*, 2011, 55: 965
- 42 Ban, L.L., Hess, W.M. and Papazian, L.A., *Rubber Chem. Technol.*, 1974, 47: 858
- 43 Hamed, G.R. and Hatfield, S., *Rubber Chem. Technol.*, 1989, 62: 143
- 44 Moldovan, D., Fechete, R., Demco, D.E., Culea, E., Blümich, B., Herrmann, V. and Heinz, M., *J. Magn. Reson.*, 2011, 208: 156
- 45 Fang, X.L., Huang, X., Lu, Z., Chen, L. and Chen, S., *Polym. Compos.*, 2010, 31: 1628
- 46 Mujumdar, A., Beris, A.N. and Metzner, A.B., *J. Non-newton. Fluid Mech.*, 2002, 102: 157
- 47 Aranguren, M.I., Mora, E., DeGroot, J.V. and Macosko, C.W., *J. Rheol.*, 1992, 36: 1165
- 48 Bailly, M. and Kontopoulou, M., *J. Rheol.*, 2013, 57: 407
- 49 Vermant, J., Ceccia, S., Dolgovskij, M.K., Maffettone, P.L. and Macosko, C.W., *J. Rheol.*, 2007, 51: 429
- 50 Piau, J. M., Dorget, M. and Palierne, J.F., *J. Rheol.*, 1999, 43: 305

- 51 Allegra, G., Raos, G. and Vacatello, M., *Prog. Polym. Sci.*, 2008, 33: 683
- 52 Sun, J., Song, Y., Zheng, Q., Tan, H., Yu, J. and Li, H., *J. Polym. Sci., Part B: Polym. Phys.*, 2007, 45: 2594
- 53 van de Walle, A., Tricot, C. and Gerspacher, M., *Kautsch. Gummi Kunstst.*, 1996, 49: 172
- 54 Yang, R., Song, Y. and Zheng, Q., *Polymer*, 2017, 116: 304
- 55 Yin, X., Tan, Y., Chen, Y., Song, Y. and Zheng, Q., *Polym. Int.*, 2012, 61: 1439
- 56 Yin, X., Tan, Y., Gao, Y., Song, Y. and Zheng, Q., *Polymer*, 2012, 53: 3968
- 57 Yin, X., Tan, Y., Li, L., Song, Y. and Zheng, Q., *Acta Polymerica Sinica (in Chinese)*, 2012, (11): 1335
- 58 Zhao, L., Yang, H., Song, Y., Zhou, Y., Hu, G. and Zheng, Q., *J. Mater. Sci.*, 2010, 46: 2495
- 59 Rooj, S., Das, A., Stoeckelhuber, K.W., Wang, D.Y., Galiatsatos, V. and Heinrich, G., *Soft Matter*, 2013, 9: 3798
- 60 Kraus, G., *Appl. Polym. Symp.*, 1984: 75
- 61 Chazeau, L., Brown, J.D., Yanyo, L.C. and Sternstein, S.S., *Polym. Compos.*, 2000, 21: 202
- 62 Sternstein, S.S. and Zhu, A.J., *Macromolecules*, 2002, 35: 7262