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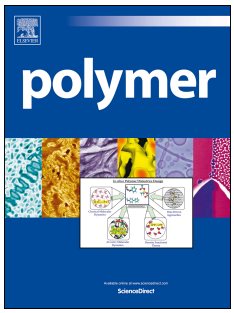


Linear rheology of natural rubber compounds filled with silica, short nylon fiber or both

Yihu Song, Dengjia Huang

PII: S0032-3861(17)31141-2

DOI: 10.1016/j.polymer.2017.11.073

Reference: JPOL 20186

To appear in: *Polymer*

Received Date: 12 October 2017

Revised Date: 25 November 2017

Accepted Date: 27 November 2017

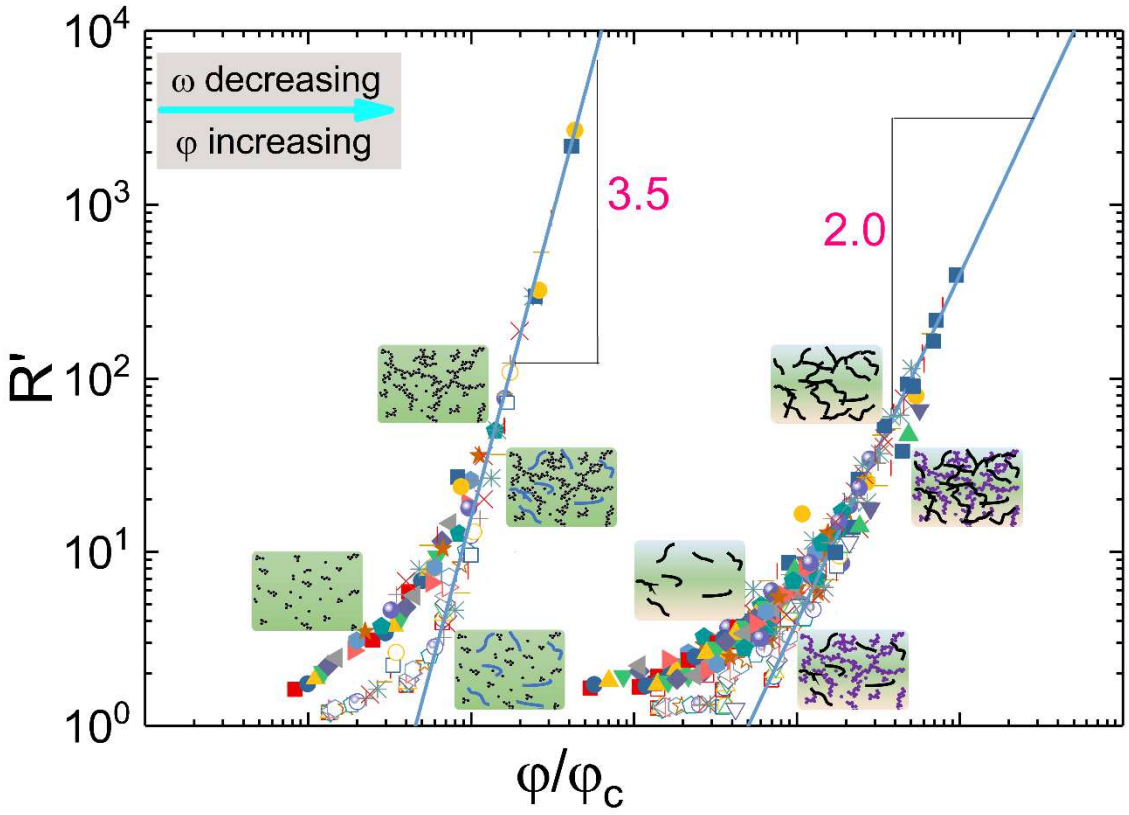
Please cite this article as: Song Y, Huang D, Linear rheology of natural rubber compounds filled with silica, short nylon fiber or both, *Polymer* (2017), doi: 10.1016/j.polymer.2017.11.073.

Graphical Abstract

Linear rheology of natural rubber compounds filled with silica, short nylon fiber or both

Yihu Song, Dengjia Huang, Qiang Zheng

The time-concentration superpositioning principle is able to account for the reinforcement and dissipation of natural rubber filled with silica, short nylon fiber or both.



Linear rheology of natural rubber compounds filled with silica, short nylon fiber or both

Yihu Song*, Dengjia Huang

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

RUNNING TITLE: Linear rheology of NR compounds

* Corresponding author.

E-mail address: s_yh0411@zju.edu.cn (Y. Song).

Abstract: Engineered rubbery materials in practical applications usually contain nanoparticle and microscopic short fiber while no theories could describe the viscoelasticity of the compounds varying with these two kinds of fillers. We describe how the linear rheology of natural rubber compounds varies with the loading of precipitated silica, short nylon fiber, or both. We for the first time disclose a filler dimension-dependent hydrodynamic-to-non-hydrodynamic transition by applying the time-concentration superposition principle for accounting for the apparent liquid-to-solid transition related to filler composition and loading and the retarded dynamics of the matrix. A framework for simultaneous solving the reinforcement and dissipation of the multi-component compounds is suggested, providing a new perspective on understanding the filling effect for manufacturing high-performance rubber materials.

Keywords: Compounds; Rheology; Time-concentration superposition

Nanoparticles are extensively used to reinforce rubbers [1-4]. In engineered truck tread compounds, a low content of well dispersed short fibers is usually introduced to improve mechanical and dynamic properties. Both nanoparticles and short fibers could introduce a so-called liquid-to-solid transition that is importance for optimizing the compounding behaviors for developing high-performance materials for tires and other applications [5, 6]. While a range of efforts have been made to understand the filler reinforcement behavior in myriad publications in the open literature, few studies are focused on the synergistic effect of nanoparticles and microfibers on the linear rheology of the multi-component compounds [7] and there are lack of theories being able to predict the compounds' viscoelasticity as a function of filler composition and polymer dynamics. Herein we prepare natural rubber (NR) compounds filled with precipitated silica (PS), short nylon fiber (SNF) or both fillers. We investigate the rheological roles played by nanoparticles and microfibers for providing a better understanding of the reinforcement and dissipation mechanisms.

We prepared single- and two-filler compounds of NR (SVR3L, weight-averaged molecular weight 1,120 kg mol^{-1}, polydispersity index 3.57, polyisoprene content 98 %, Shanghai Duokang Ind. Co., Ltd., China) according to the formulations listed in Table 1. The single-filler compounds PS(NR) were prepared by mixing NR, PS (ZQ356; cetyltrimethyl ammonium bromide adsorption 184 m^2 g^{-1}, dibutyl phthalate adsorption 5.5 cm^3 g^{-1}, Zhuzhou Xinglong Chem. Ind. Co., Ltd., China), and silane bis(*γ*-triethoxysilylpropyl)tetrasulfide (5 % in mass with respect to PS, Hangzhou Jessica Chem. Co., Ltd., China) in a torque rheometer (HAAKE, Thermo Scientific Co., USA) at 150 °C and 60 rpm for 12 min. The two-filler compounds PS(SNF0.014) were prepared following the aforementioned procedure but a predetermined amount of $SNF(NR)_c$ was incorporated. The single-filler compounds $SNF(NR)_{uc}$ were prepared by mixing NR and short fibers of nylon 66 (N3/30, 3.0 ± 0.3 mm in length, aspect ratio 160, Goonvean Fibres Ltd., UK) at 50 °C for 12 min on a two-roll open mill (XK-160, Zhanjiang Rubber & Plastic

Machinery Co., Ltd., China). The single-filler compounds SNF(NR)$_c$ containing maleated natural rubber by an amount of 10 parts per hundred NR were prepared following the same procedure. The single-filler compounds SNF(NR)$_c$ with φ_{SNF}=0.07 was diluted by NR to produce SNF(NR)$_d$. During the dilution procedure, the single-filler compound PS(NR) with φ_{SNF}=0.20 was introduced, yielding the two-filler compounds SNF(PS0.12)$_d$. Antioxidant *N*-(1,3-dimethylbutyl)-*N*'-phenyl-*p*-phenylenediamine (Changzhou Xince Polym. Mater. Co., Ltd., China) by an amount of 1.6 parts per hundred NR was included in all the compounds.

Table 1. The filler compositions and main rheological parameters of the compounds.

Compounds [a]	φ_{PS}	φ_{SNF}	τ_m (s) [b]	φ_{cm} [c]
PS(NR)	0.04-0.20	0	0.01566	0.410
PS(SNF0.014)	0.04-0.20	0.014	0.15659	0.160
SNF(NR)$_{uc}$	0	0.07-0.28	0.07937	0.340
SNF(NR)$_c$	0	0.07-0.28	0.05682	0.290
SNF(NR)$_d$	0	0.014-0.070	0.03472	0.165
SNF(PS0.12)$_d$	0.12	0.014-0.070	0.14706	0.087

[a] The compounds are named as A(B) where A and B denote the filler and matrix. The latter may be either pure rubber (NR) or filled rubber (SNF0.014 and PS0.12, containing 1.4% SNF and 12% PS in volume fractions, respectively). The subscripts "uc" and "c" identify the uncompatibilized compounds and those compatibilized with maleated natural rubber with 1.5% grafted maleic anhydride prepared *via* a Nakason method [8]. The subscript "d" denotes the compounds prepared via the dilution method. [b] Terminal relaxation time of the matrix determined at reciprocal of frequency at the $G'_m(\omega)$-$G''_m(\omega)$ crossover for the single-filler compounds or by applying the modified two phase model for the two-filler compounds. [c] Critical concentration for hydrodynamic-to-non-hydrodynamic regime transition at $\omega=1/\tau_m$.

The compounds after storage for more than one day were compressed into discs of 25 mm in diameter and 2 mm in thickness on a press vulcanizer (XL-25, Huzhou Xinli Rubber Machinery Co., Ltd., China) at 100 ± 5 °C under 10 MPa for 10 min. A strain-controlled rheometer (ARES-G2, TA Instrument, USA) was used to measure dynamic rheological responses of the uncured compounds at 100 °C using a plate-plate geometry with a serrated surface texture to prevent slipping. Frequency (ω) sweeps from 100 to 0.0158 rad s^{-1} were performed at 0.1 % dynamic strain amplitude located in the linearity regime (Fig. S1).

By introducing maleated natural rubber as compatibilizer and silane as coupling agent, both SNF and PS are well dispersed (Fig. S2). While both fillers do not influence glass transition temperature of the mobile rubber component (Fig. S3), they cause the liquid-to-solid transition (Fig. 1) as identified from appearance of plateaus of storage and loss moduli [$G'(\omega,\varphi)$ and $G''(\omega,\varphi)$] in the low-ω side where NR undergoes the terminal flow ($G'\sim\omega^2$, $G''\sim\omega^1$) [2, 4]. A totally solid-like rheology [$G'(\omega,\varphi) > G''(\omega,\varphi)$ within the ω range experimentally achieved] is observed for the compounds filled with PS [φ_{PS}=0.20 for the single-filler compounds PS(NR)], SNF [$\varphi_{SNF}\geq$0.14 for the single-filler compounds $SNF(NR)_{uc}$ and $SNF(NR)_c$], or both [φ_{PS}=0.20 and φ_{SNF}=0.014 for the two-filler compounds PS(SNF0.014); φ_{PS}=0.12 and φ_{SNF}=0.07 for the two-filler compounds $SNF(PS0.12)_d$]. Both the uncompatibilized and compatibilized single-filler compounds, $SNF(NR)_{uc}$ and $SNF(NR)_c$, show the solid-like rheology at the same φ_{SNF} range while the single-filler compounds prepared via the dilution method, $SNF(NR)_d$, demonstrate the liquid-like rheology due to the low SNF loadings. The liquid-to-solid transition induced by nanosized PS can be ascribed to the networking of nanoparticles interconnected by chain bridges [9-15]. In the SNF compounds, it could also be induced by the formation of a physical fiber network [16, 17].

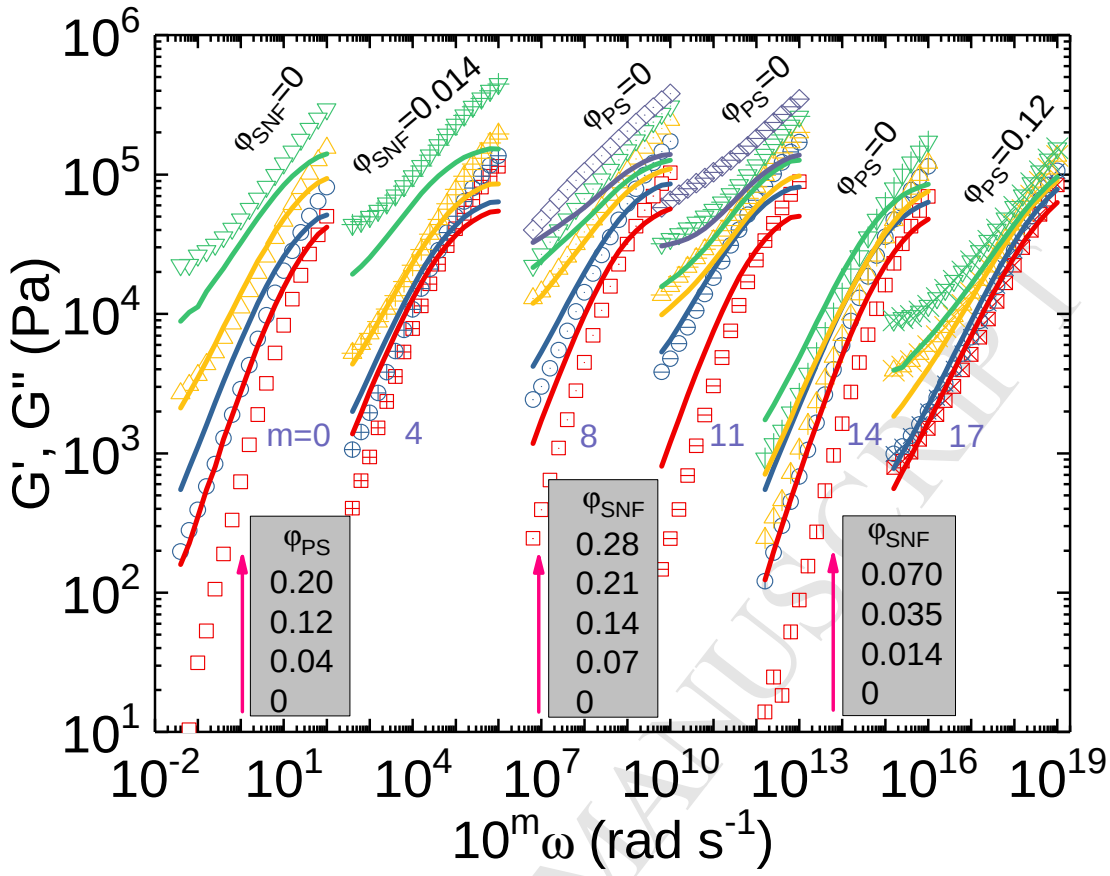


Fig. 1. Dynamic moduli $G'(\omega,\varphi)$ (symbols) and $G''(\omega,\varphi)$ (curves) as a function frequency ω for PS(NR), PS(SNF0.014), SNF(NR)$_{uc}$, SNF(NR)$_c$, SNF(NR)$_d$, and SNF(PS0.12)$_d$ from the left to right. The fillers volume fractions are indicated. The data are horizontally shifted by a factor of 10^m for a clear comparison of the linear rheology of the different compounds.

For the single-filler compounds, both PS and SNF reinforce the NR matrix, as shown in Fig. 2a and b where relative dynamic moduli, $R'(\omega,\varphi)=G'(\omega,\varphi)/G'_m(\omega)$ and $R''(\omega,\varphi)=G''(\omega,\varphi)/G''_m(\omega)$, are plotted as a function of ω. Here $G'_m(\omega)$ and $G''_m(\omega)$ are storage and loss moduli, respectively, of the matrix. At given φ, both $R'(\omega,\varphi)$ and $R''(\omega,\varphi)$ decrease with increasing ω and $R''(\omega,\varphi)$ is always lower than $R'(\omega,\varphi)$. For the two-filler compounds, the first type of filler (varying loadings) could also reinforce the filled NR matrix (NR filled with the second filler at a constant loading), as shown in Fig. 2c and d. Furthermore, both $R'(\omega,\varphi)$ and $R''(\omega,\varphi)$ become nearly ω-independent in the high-ω hydrodynamic limit, which is more marked for the two-

filler compounds at low φ. The results presented in Fig. 2 reveal a filling-induced hydrodynamic to non-hydrodynamic transition with increasing φ and decreasing ω. This transition is undoubtedly strongly influenced by the filler type and composition. It is clear that both $R'(\omega,\varphi)$ and $R''(\omega,\varphi)$, characterizing the increments of dynamic moduli of the two-filler compounds over the filled NR matrix, are lower than those in the single-filler compounds. For example, the reinforcement effect of PS in the two-filler compounds PS(SNF0.014) (Fig 2c) is reduced markedly in comparison with that in the single-filler compounds PS(NR) (Fig 2a), by more than one order of magnitude at φ_{PS}=0.20 at the lowest ω, which could be related to the dynamics retardation in the filled NR matrix (inset in Fig 2c). In the two-filler compounds SNF(PS0.12)$_d$ whose filled matrix (φ_{PS}=0.12) behaves critical gel-like [$G'_m(\omega)\approx G''_m(\omega)\sim\omega^{0.58}$, inset in Fig 2d] due to the filler networking [1, 2, 4], the reinforcement effect of SNF (Fig 2d) becomes much lower than that in the single-filler compounds SNF(NR)$_d$ (Fig 2b). It means that the linear rheology of the compounds is strongly influenced by the dynamics of the (filled) matrix.

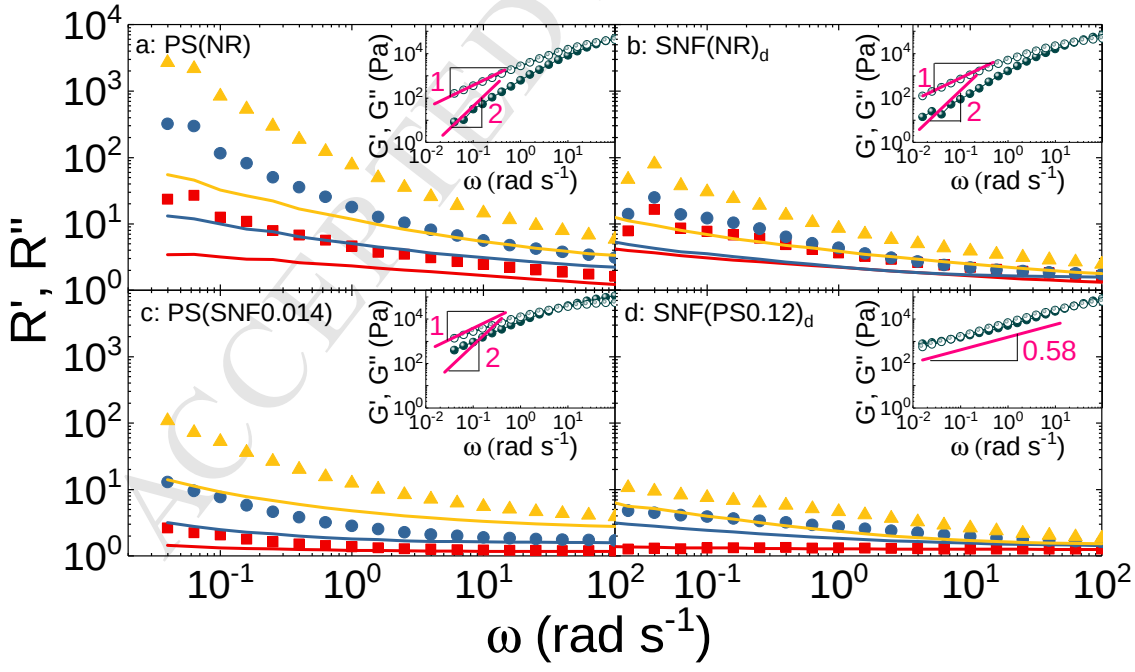


Fig. 2. Relative dynamic moduli R' (solid symbols) and R'' (curves) as a function frequency ω for PS(NR) (a, φ_{PS}=0.04, 0.12, and 0.20, from bottom to top), SNF(NR)$_d$ (b, φ_{SNF}=0.014, 0.035 and 0.070, from bottom

to top), PS(SNF0.014) (c, φ_{PS}=0.04, 0.12, and 0.20, from bottom to top) and SNF(PS0.12)$_d$ (d: φ_{SNF}=0.014, 0.035 and 0.070, from bottom to top). The insets show linear rheology of the (filled) matrix, indicating the deviation from classic terminal flow law.

While $R'(\omega,\varphi)$ is usually used to semiempirically discuss the reinforcement mechanism in relation to hydrodynamic effect in the "high"-ω regime at low-φ, or the jamming effect in the "low"-ω regime at moderately high-φ [2-4, 18-20], no theory could account for $R''(\omega,\varphi)$. It is revealed recently that the liquid-to-solid transition in polymer nanocomposites in wide ranges of φ and ω can be accounted for by a time-concentration superposition principle [21-27]. This principle allows normalizing both $R'(\omega,\varphi)$ and $R''(\omega,\varphi)$ with respect to φ scaled by an ω-dependent critical filler loading $\varphi_c(\omega)$, which is validated in the compounds containing nanosized PS, microsized SNF and both. As shown in Fig. 3, $R'(\omega,\varphi)$ and $R''(\omega,\varphi)$ [shown in inset in Fig. 3 for the single-filler compounds PS(NR) as an example] are normalized onto their respective master curves by plotting against $\varphi/\varphi_c(\omega)$; the superposition does not call for any vertical shift factors even though the superposed data are somewhat scatted in a narrow range. Note that, in the whole $\varphi/\varphi_c(\omega)$ range achieved, both the reinforcement and dissipation effects in the single-filler compounds are more significant than those in the two-filler compounds (as shown in Fig. 2). The master curves of the two-filler compounds are shifted horizontally so as to overlap those of the single-filler compounds at $\varphi/\varphi_c(\omega)>1$ in the non-hydrodynamic regime. In this regime, the reinforcement obeys the unique scaling law $R'(\omega,\varphi)\sim[\varphi/\varphi_c(\omega)]^x$ predicted by the cluster-cluster aggregation model [1-4, 28-34]. Here x is a critical exponent being usually taken as 4.5 for the reaction-limited cluster-cluster aggregation (weak link regime dominated by the floc network) and 3.5 for the diffusion-limited cluster-cluster aggregation (strong link regime dominated by individual flocs) in 3D [34]. The x values of the single- and two-filler compounds, PS(NR) and PS(SNF0.014), are the same (x≈3.50±0.25),

no matter whether SNF (φ_{SNF}=0.014) is incorporated or not. Also true are the x values (x≈2.00±0.10) of the single-filler compounds SNF(NR)$_{uc}$, SNF(NR)$_c$, and SNF(NR)$_d$ and the two-filler compounds SNF(PS0.12)$_d$, regardless of whether or not PS (φ_{PS}=0.12) is incorporated. The slopes of the $R''(\omega,\varphi)$ master curves in the non-hydrodynamic regime are smaller than those of $R'(\omega,\varphi)$, being about 1.60±0.10 for the PS(NR) and PS(SNF0.014) compounds and 1.33±0.15 for SNF(NR)$_{uc}$, SNF(NR)$_c$, SNF(NR)$_d$, and SNF(PS0.12)$_d$ compounds, respectively.

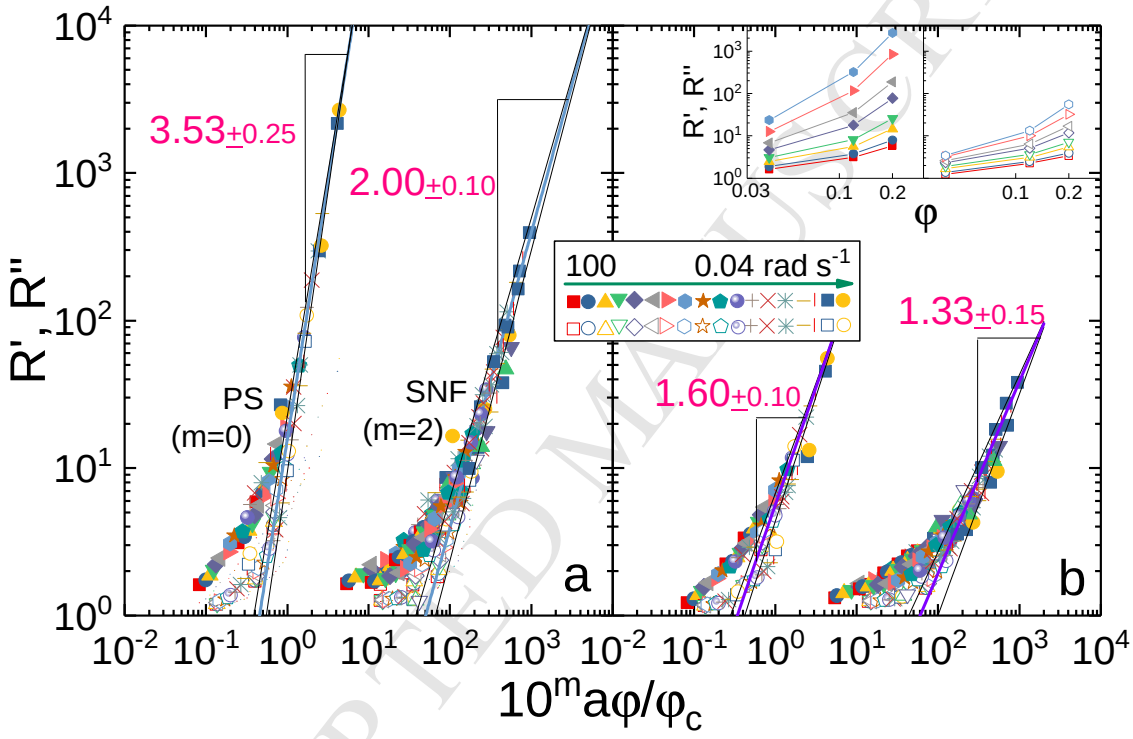


Fig. 3. Relative dynamic moduli, $R'(\omega,\varphi)$ (a) and $R''(\omega,\varphi)$ (b), as a function of φ/φ_c for the single- (filled symbols) and two-filler compounds (open symbols). The master curves are created for the compounds with varying φ and ω. The data for the single-filler compounds marked as "SNF" includes SNF(NR)$_{uc}$, SNF(NR)$_c$, and SNF(NR)$_d$. The straight lines are drawn according to the scaling law. The data for the compounds with varying SNF loadings are shifted rightward by two orders of magnitude for clear display. The data for the two-filler compounds are shifted by a factor of a for overlapping onto that of the single-filler compounds. Inset shows R' (filled symbols) and R'' (open symbols) at eight prescribed frequencies (100, 40, 10, 4, 1, 0.4, 0.1, and 0.04 rad s^{-1}, from bottom to top) as a function of φ for PS(NR).

In the time-concentration superposition approximation, $\varphi_c(\omega)$ depicts a unique ω-dependent hydrodynamic-to-non-hydrodynamic regime transition dominated by the relaxation of the matrix. $\varphi_c(\omega)$ is shown in a normalized form in Fig. 4, in which τ_m is the terminal relaxation time of pure polymer and φ_{cm} is the $\varphi_c(\omega)$ value at $\omega=1/\tau_m$ (Table 1). For the single-filler compounds, τ_m is determined at reciprocal of frequency at the $G'_m(\omega)$-$G''_m(\omega)$ crossover; for the two-filler compounds, τ_m is determined according to the modified two phase model applied to the filled NR matrix [24]. It is interesting that the normalized plot of $\varphi_c(\omega)/\varphi_{cm}$ against $\omega\tau_m$ is sensitive to the filler composition rather than the processing method. For the single-filler compounds, $\varphi_c(\omega)/\varphi_{cm}$ scales like $(\omega\tau_m)^{0.29}$ for PS and $(\omega\tau_m)^{0.38}$ for SNF. For two-filler compounds in which the polymer dynamics are retarded markedly, $\varphi_c(\omega)/\varphi_{cm}$ levels off in the hydrodynamic regime at $\omega\tau_m>1$ while it is higher than those of the single-filler compounds at $\omega\tau_m<1$. The scaling behavior observed at high φ (Fig. 3) works only when the matrix relaxes fully in the low-ω region. In comparison with the single-filler compounds, the coexistence of PS and SNF would facilitates the hydrodynamic-to-non-hydrodynamic regime transition due to the dynamics retardation effect (Table 1).

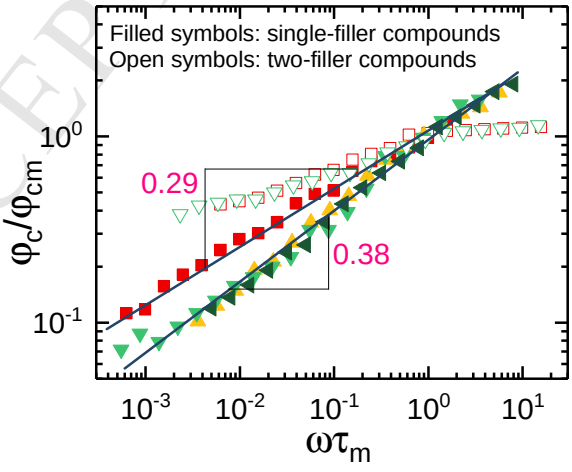


Fig. 4. Normalized critical filler loading $\varphi_c(\omega)/\varphi_{cm}$ as a function of normalized frequency $\omega\tau_m$ for PS(NR) (filled square), PS(SNF0.014) (open square), SNF(NR)$_{uc}$ (filled left-triangle), SNF(NR)$_c$ (filled up-triangle),

SNF$(NR)_d$ (filled down-triangle), and SNF$(PS0.12)_d$ (open down-triangle).

In conclusion, both PS and SNF induce the apparent liquid-to-solid transition. Despite of dimensional differences in the two fillers, this transition could be well accounted for by the time-concentration superposition principle. The roles of filler are found here to be dual. Filler invariably retards the dynamics of the mobile rubber phase while the coexistence of two types of fillers could accelerate the liquid-to-solid transition. However, the presence of one type of filler does not influence the reinforcement and dissipation effects associated with another type of filler.

Acknowledgements

This work was partially supported by the National Natural Science Foundation of China (Grant No. 51573157, 51333004, and 51373149), the Natural Science Foundation of Zhejiang Province, China (Grant No. R14E030003), and the Major Projects of Science and Technology Plan of Guizhou Province, China (Grant No. (2013) 6016).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.polymer.2017.**. ***.

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Highlights

- Viscoelasticity of natural rubber compounds varies with nanosilica and microscopic short nylon fiber.
- Linear rheology of the compounds follows time-concentration superpositioning principle.
- The rheological contributions of nanosilica and short nylon fibers are independent of each other.