

Nonlinear Stress Relaxation of Silica Filled Solution-Polymerized Styrene–Butadiene Rubber Compounds

Jin Sun,^{1,2} Hong Li,¹ Yihu Song,¹ Qiang Zheng,^{1,2} Li He,² Jie Yu²

¹Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, China 310027

²National Engineering Research Center for Compounding and Modification of Polymeric Materials, Guiyang, China 550025

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ABSTRACT: The stress relaxation of silica (SiO₂) filled solution-polymerized styrene–butadiene rubber (SSBR) has been investigated at shear strains located in the nonlinear viscoelastic regions. When the characteristic separability times are exceeded, the nonlinear shear relaxation modulus can be factorized into separate strain- and time-dependent functions. Moreover, the shear strain dependence of the damping function becomes strong with an increase in the SiO₂ volume fraction. On the other hand, a strain amplification factor related to nondeformable SiO₂ particles can be applied to account for the local strain of the rubbery matrix. Furthermore, it is believed that the damping function is a function of the localized deformation of the rubbery matrix

independent of the SiO₂ content. The fact that the time–strain separability holds for both the unfilled SSBR and the filled compound indicates that the nonlinear relaxation is dominated by the rubbery matrix, and this implies that the presence of the particles can hardly qualitatively modify the dynamics of the polymer. It is thought that the filler–rubber interaction induces a coexistence of the filler network with the entanglement network of the rubbery phase, both being responsible for the nonlinear relaxation. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3569–3574, 2009

Key words: relaxation; rubber; silicas; viscoelastic properties

INTRODUCTION

The desire to improve rolling resistance, traction, and wet-sliding friction has promoted the application of silica (SiO₂) in tire treads.^{1–5} At temperatures far above the glass-transition temperature, filled rubber compounds generally exhibit nonlinear rheological behavior that is of great practical significance in their processing for the rubber industry. First of all, this requires a precise description of how filler particles modify the rheological properties of the unfilled rubber.⁶

It is well known that most polymers exhibit nonlinear viscoelastic behavior under relatively large strains,^{7–13} and step deformations are a critical test for the rheological properties of polymers. At a sufficiently long time after a step, the stress response invariably indicates time–strain separability,¹⁴ that is, factorization of the relaxation moduli into a strain-dependent damping function [$h(\gamma)$] and a time-dependent relaxation function [$G_0(t)$]. Doi and Edwards¹⁵ employed the reptation concept to model the viscoelastic behavior as retraction along the tube

of a chain extended in large deformation, which could qualitatively describe the relaxation behavior of monodisperse polymers. Osaki¹⁶ characterized the step-shear damping function of polystyrene solutions with entanglement densities (N/N_e) greater than 50 as type C damping because their long-time damping behavior is substantially more strain-softening (particularly at low strains) than the prediction of the Doi–Edwards constitutive theory. Conversely, $h(\gamma)$ for polymers with weak and moderate entanglement densities or high polydispersity indices is generally in accord with the Doi–Edwards predictions and has been termed type A damping. However, the switch from of type A damping to type C damping at high entanglement densities is obviously perplexing.^{17–19} Partly from the standpoint of the Doi–Edwards theory, Takahashi et al.²⁰ examined the nonlinear viscoelasticity of ABS polymers containing well-dispersed rubber particles. ABS polymers exhibit a different relaxation process related to the motion of chain segments with various lengths and rubber particles. Concerning filled polymers, several works mentioning time–strain separability have dealt with glass beads in polydimethylsiloxane,¹⁴ carbon black or SiO₂ particles in styrene–butadiene rubber,^{21,22} and organically modified montmorillonite in a disordered styrene–isoprene diblock copolymer.²³

In our previous article,²⁴ we used the concept of strain amplification to interpret the Payne effect of

Correspondence to: Q. Zheng (zhengqiang@zju.edu.cn).

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SiO₂ filled solution-polymerized styrene-butadiene rubber (SSBR). The Payne effect in filled elastomers refers to the reduction of the dynamic storage modulus with increasing strain amplitude above a critical value. It was found that the Payne effect was primarily involved in the entanglement network in the rubbery matrix, and the cooperation between the breakdown-reformation of the filler network and the molecular disentanglement of the matrix resulted in an enhancement of the Payne effect and improved the mechanical hysteresis at high strain amplitudes. In this article, we further probe the shear stress relaxation behavior of SiO₂-filled SSBR in the nonlinear viscoelastic regions to examine the applicability of the strain amplification concept to the relaxation dynamics of filled rubbers.

EXPERIMENTAL

Materials

SSBR (PR1205) with a styrene content of 25% and a glass-transition temperature of -67°C (based on dynamic mechanical analysis measurements taken with a TA Q800 dynamic mechanical analyzer at $5^{\circ}\text{C}/\text{min}$) was obtained from Chimei Co. (China). Precipitated SiO₂ (Ultrasil VN3 GR) with a specific surface area of $175\text{ m}^2/\text{g}$ was obtained from Degussa Co. The average particle size of SiO₂ was calculated with a statistical Ferret diameter and was found to be about 27 nm.²⁵ 3-Octanoylthio-1-propyltriethoxyl silane, provided by Crompton Co., was used as a coupling agent to facilitate filler dispersion. Other additives such as stearic acid, wax, zinc oxide, and an antioxidant N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) were provided by Jinghui Co. (China).

Sample preparation

Filled rubber compounds were formulated with 100 weight parts of SSBR and different amounts (0, 10, 30, and 50 parts) of the filler. The volume fraction of the filler in these stocks was 0, 0.04, 0.12, and 0.20, respectively. The ingredients, following the recipe listed in Table I, were mixed with a two-roll mill (Tiancan Instrument Co., China) at 50°C and then blended in a Haake rheometer (ThermoFisher Scientific Co., USA) at 150°C and 30 rpm for 10 min. The resultant compounds were compressed at 150°C and 10 MPa into discs 25 mm in diameter and 1.5 mm thick.

Dynamic rheological measurements

Dynamic rheological measurements were performed on an Advanced Rheometric Expanded System (TA Instrument Co., USA) with strain, frequency, and

TABLE I
Formulations of the Compounds

Ingredient	phr
SSBR	100
SiO ₂	Variable
Silane coupling agent	Corresponds to the SiO ₂ loading
Zinc oxide	2.5
Stearic acid	1
Antioxidant (6PPD)	2
Wax	1.5

transient shear stress relaxation sweep modes. Toothed clamps were used to enhance the friction between the metal plate and the polymeric composite melt. To ascertain the linear viscoelastic region of the compounds, the strain sweep test was conducted at a frequency of 1 s^{-1} with the variation of strain amplitude γ from 0.01 to 100%. The stress relaxation experiment was performed in the γ range of 1–300%. All rheological properties were measured at 150°C , which was much higher than the glass-transition temperature of SSBR.

RESULTS AND DISCUSSION

Figure 1 shows the nonlinear shear relaxation modulus [$G(t, \gamma)$] at various γ values for the compounds with various filler concentrations. It is clear that $G(t, \gamma)$ decreases with increasing time t and γ . The nonlinear relaxation of homopolymers generally obeys the principle of time-strain factorability, and $h(\gamma)$ can be determined by the vertical shifting of $G(t, \gamma)$ in the long relaxation time region.^{26,27}

$$h(\gamma) = G(t, \gamma)/G_0(t, \gamma \rightarrow 0) \quad \text{for } t > \lambda_k \quad (1)$$

where $G_0(t, \gamma \rightarrow 0)$ is the linear stress relaxation modulus and λ_k is the separability time. Figure 2 provides the $G(t, \gamma)$ data, which have been shifted vertically to be superposed on the reference curve at the smallest value of γ (1%) located in the linear viscoelastic region. There is a breakdown of time-strain superpositioning at short times. However, good superpositioning is approximately gained in the medium time region ($t_k < t < 100\text{ s}$). The arrow in the figure indicates the value of λ_k beyond which nonlinear moduli can be factorized approximately into separate strain- and time-dependent functions. In this case, the time required for $h(\gamma)$ to achieve its long-time value is λ_k . λ_k decreases with an increase in the filler concentration.

Recent studies^{28,29} using NMR techniques have essentially confirmed that in a well-dispersed uncured compound, isolated aggregates restrict the mobility of rubber chains in such a manner that three rubber regions can be distinguished. NMR relaxation experiments reflect the heterogeneity of the filled rubbers. A fast decay in the 20- μs range is

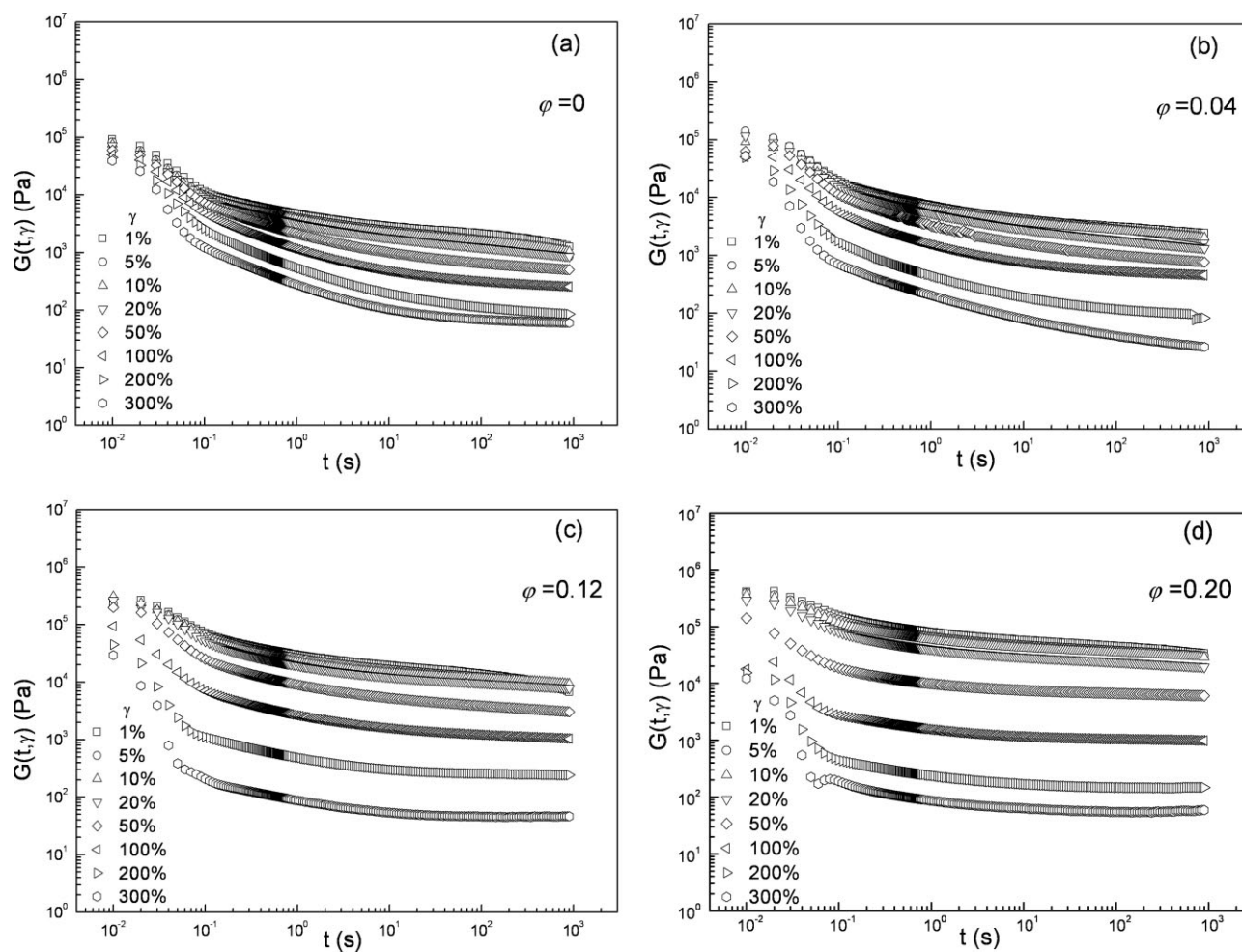


Figure 1 $G(t, \gamma)$ as a function of time t at 150°C and different values of γ for SiO_2/SSBR compounds with various filler concentrations.

assigned to the immobilized part of the bound rubber. At longer times ($>100 \mu\text{s}$), there is a mobile fraction that contributes to the relaxation, and between them (in the 50- μs range), there is an intermediate mobility component. An uncured filled elastomer compound can thus be viewed as an interpenetrated network. Complex rubber–filler units self-organize in a soft, highly deformable network that is interpenetrated by the extractable polymer, whose rheological behavior is controlled by entanglements. It also can be considered that the addition of filler blocks entangles the rubbery chain and accelerates the relaxation of the matrix. In the filled compounds, the filler–rubber interaction induces a coexistence of the filler network with the entanglement network of the rubbery phase. The time-dependent stress relaxation of the polymer is involved in two relaxation processes. The fast process arises from the relaxation of molecular stretching, and the slow process reflects the relaxation of molecular orientation.¹⁵ Archer and coworkers^{30,31} found that although the fast process is dominated by relaxation of polymer chain stretch-

ing, the second process includes both stretching and orientation relaxation contributions.

Figure 3 depicts $h(\gamma)$ as a function of γ for SiO_2/SSBR compounds with various filler concentrations. $h(\gamma)$ is independent of the SiO_2 volume fraction (ϕ) in the linear viscoelastic region, whereas it decreases rapidly with increasing γ in the nonlinear viscoelastic region. The γ dependence of $h(\gamma)$ becomes stronger with increasing ϕ . These phenomena also occur for noncolloidal particles.¹⁴

In general, the presence of a soft and highly deformable rubbery matrix and hard and much less deformable filler particles leads to a hydrodynamic effect referring to a strain amplification factor,³² which has been realized in filled elastomers subjected to stretching deformation.³³ A strain amplification effect has been introduced for investigating the influence of rigid particles on the Payne effect of filled SSBR.²⁴ When the filled compounds are sheared by a macroscopic strain amplitude, the corresponding microscopic deformation is highly inhomogeneous. Because the rigid filler particles do not

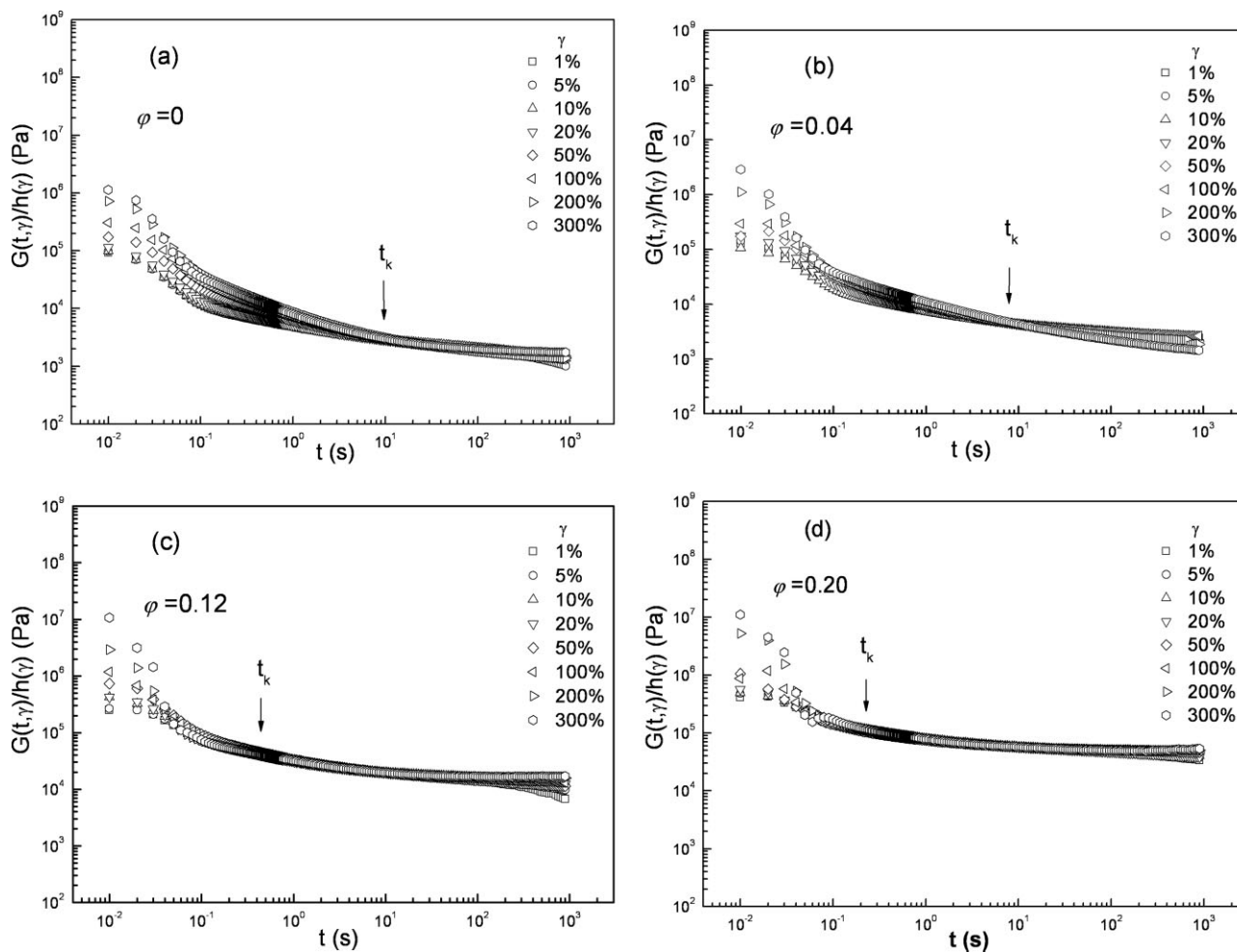


Figure 2 Master curve for the time evolution of $G(t,\gamma)$ at 150°C for SiO₂/SSBR compounds with various filler concentrations.

contribute to the global deformation, the local strain (γ_{local}) of the rubbery matrix between particles is considerably larger than γ . In the shear deformation, the strain amplification factor is defined as $A(\phi) =$

γ_{local}/γ ,³⁴ and γ_{local} of the rubbery phase can be obtained as $\gamma_{local} = A(\phi)\gamma$. Figure 4 shows $h(\gamma_{local})$ as a function of $A(\phi)\gamma$, taking $A(\phi)$ as an adjusting

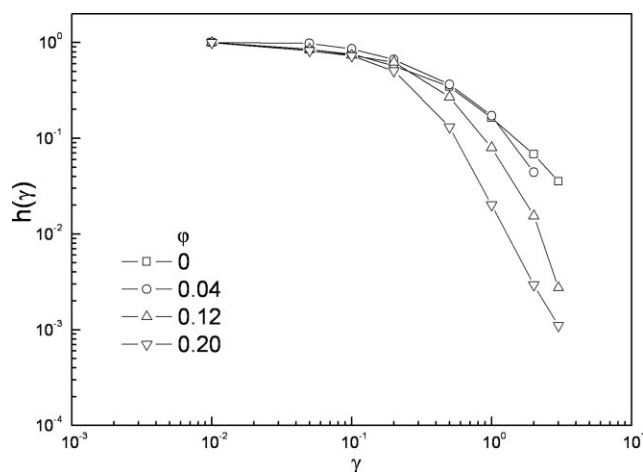


Figure 3 $h(\gamma)$ as a function of γ at 150°C for SiO₂/SSBR compounds with various filler concentrations.

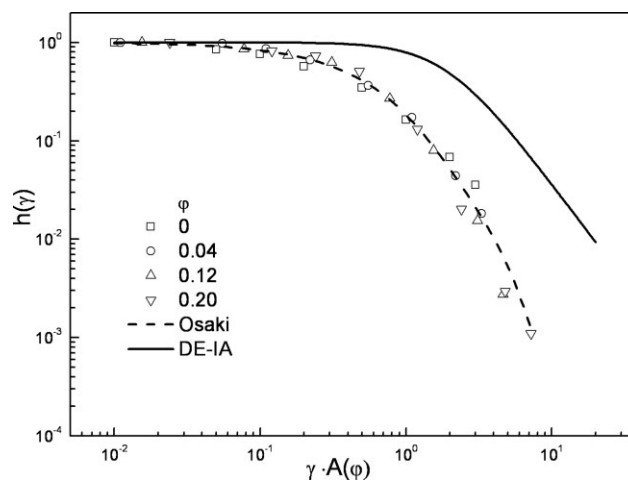


Figure 4 Master curve for $h(\gamma)$ as a function of modified shear strain $\gamma A(\phi)$ at 150°C for SiO₂/SSBR compounds with various filler concentrations (DE-IA: Prediction of the Doi–Edwards theory).

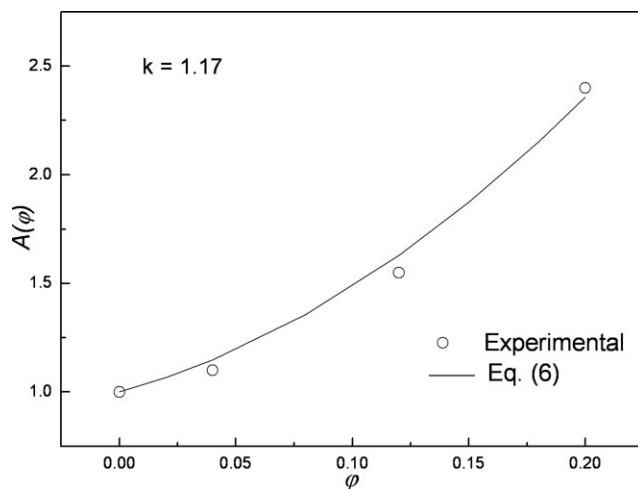


Figure 5 $A(\phi)$ as a function of ϕ at 150°C for SiO₂/SSBR compounds.

parameter so that the data of the filled compound can be superposed onto that of pure SSBR. The decay of $h(\gamma_{\text{local}})$ is faster than the prediction of the Doi–Edwards theory with the independent alignment approximation ($h_{\text{DE-IA}}$)¹⁵:

$$h_{\text{DE-IA}} = \frac{1}{1 + (4/15)\gamma_{\text{local}}^2} \quad (2)$$

On the other hand, $h(\gamma_{\text{local}})$ follows the prediction by the Osaki-type double exponential equation (h_{Osaki}) over the range of shear strains tested (as shown by the dashed curve)¹⁶:

$$h_{\text{Osaki}} = \beta \exp(-n_1\gamma_{\text{local}}) + (1 - \beta) \exp(-n_2\gamma_{\text{local}}) \quad (3)$$

where β , n_1 , and n_2 are parameters. This type of damping behavior has previously been characterized as type C damping by Osaki for highly entangled polymers. The trend toward type C damping increases with the filler concentration.

Figure 5 demonstrates the value of $A(\phi)$ as a function of ϕ . An increase in $A(\phi)$ with ϕ reveals that the filler loading facilitates the increase in the strain amplification effect in the rubbery phase. The Guth–Gold equation, based on simple geometrical considerations,³⁵ can well describe $A(\phi)$ as a function of ϕ :

$$A(\phi) = 1 + 2.5(k\phi) + 14.1(k\phi)^2 \quad (4)$$

Here, the parameter k takes into account the effective volume fraction for the particles surrounded by bound rubber. Moreover, eq. (4) can be applied to fit $A(\phi)$ in Figure 5, and the satisfactory fitting result with $k = 1.17$ is presented as a solid curve.

The results reveal that the time–strain separability holds for both the unfilled SSBR and the filled compound beyond λ_k . It implies that the presence of the

particles can hardly qualitatively modify the dynamics of the polymer. The filler–rubber interaction induces a coexistence of the filler network with the entanglement network of the rubbery phase. The molecular relaxation via reptation and disentanglement is thus enhanced in the presence of a hard filler, which causes the reduction in λ_k and the more pronounced $h(\gamma)$ value with increasing filler content. Nevertheless, $h(\gamma)$ of the filled compound is exclusively related to local deformation of polymer chains.

CONCLUSIONS

The stress relaxation behavior of SiO₂ filled SSBR compounds has been studied in the nonlinear viscoelastic regions. The time–strain separability of the relaxation modulus beyond λ_k has been verified in the medium time region. λ_k decreases with increases in the filler concentration, and the strain dependence of $h(\gamma)$ become stronger with increasing ϕ . The strain amplification effect can also be applied to demonstrate the effect of the SiO₂ filler on the nonlinear stress relaxation behavior, and this implies that the presence of the hard particles can hardly modify the dynamics of the polymer. On the other hand, $h(\gamma)$ of the filled compound is exclusively related to local deformation of polymer chains.

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