

Strain Softening of Styrene-Isoprene-Styrene Copolymers under Large Amplitude Oscillatory Shear for Clarifying Payne Effect in Rubbers and Their Nanocomposites

Xin-Peng Fan^a, Yi-Hu Song^{a,b,c*}, Qiang Zheng^{a,b}, and Wan-Jie Wang^c

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

^b Shanxi-Zheda Institute of New Materials and Chemical Engineering, Taiyuan 030000, China

^c College of Materials Science and Engineering, Henan Key Laboratory of Advanced Nylon Materials and Application, Zhengzhou University, Zhengzhou 450001, China

Electronic Supplementary Information

Abstract To illustrate mechanisms of Payne effect in rubbers and their nanocomposites experiencing large amplitude oscillatory shear (LAOS), comparison studies were performed in styrene-isoprene-styrene (SIS) copolymers and their selectively crosslinked materials at temperatures below and above glass transition temperature of the polystyrene (PS) phase. It was found that under periodic dynamic shear, the strain softening is reversible when the polyisoprene (PI) phase, either crosslinked or not, is restricted by hard PS domains but it shows hysteresis once the PS domains disassociate. The strain softening can happen at the time scale of intrinsic Rouse relaxation of elastically active network strands. Critical stress of strain softening scales with number density of elastically active network strands, a simple relation being verified not only in the selectively crosslinked SIS copolymers but also in PI gum vulcanizates and carbon black filled PI compounds. Payne effect is traditionally used to term strain softening of highly filled rubber vulcanizates under LAOS deformation while evidenced herein is that the Payne effect of highly filled rubber vulcanizates shares the mechanism being common to the strain softening of SIS copolymers.

Keywords Large amplitude oscillatory shear; SIS; Rubber nanocomposites; Strain softening

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INTRODUCTION

Strain softening of highly filled vulcanizate nanocomposites under large amplitude oscillatory shear (LAOS) is firstly investigated systematically by Payne *et al.* in the 1960s and it nowadays is termed as Payne effect.^[1,2] There is no a general consensus about its mechanisms so far. In highly filled nanocomposites where significant reinforcement is achieved due to the presence of fractal filler clusters, Payne effect is generally assigned to breakdown of clusters^[3–6] in phenomenological network models.^[7] This viewpoint is so popular even though it could not explain the strain softening of uncrosslinked and crosslinked rubbers (gum and vulcanizates) and the inconsistency between the reversible Payne effect and irreversible breakdown of filler cluster under LAOS.^[8] Being similar to rubber nanocomposites, thermoplastic copolymers formed by well entangled rubbery blocks in between glassy blocks^[9] and thermoplastic vulcanizates composed by a

semicrystalline thermoplastic polymer and discrete vulcanized rubbery domains^[10,11] are expected to exhibit severe strain softening under LAOS. The Payne effect-like behavior is assigned to disruption of the hard domain structure in thermoplastic copolymers^[9] or disintegration of agglomerated rubber domains and their debonding from the semicrystalline matrix in thermoplastic vulcanizates.^[11] Other studies focused on the shear induced breakdown of elastically active chain network such as the destruction of rubber-filler interaction^[12,13] and disentanglement of chains at the interface/bulk phase.^[14,15] However, when the chain reptation is largely suppressed in end-linking systems,^[16] the Payne effect still occurs. Furthermore, strain softening occurs in diversified material systems, including, but not limited to, homopolymer melts,^[17] hydrogels,^[18] and suspensions,^[19] which calls for investigation into the general mechanisms.

It is realized for a long time that any interpretation based on the disintegration of the so-called “filler network”^[10] meets insurmountable difficulties in explaining the rheological non-linearity^[16] especially for the rubber gums^[20,21] and their unfilled vulcanizates.^[21,22] It is recently discussed that the viscoelastic matrix undergoing amplified microscopic deforma-

* Corresponding author, E-mail: s_yh0411@zju.edu.cn

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tion is critical for nonlinear behaviors. Rigid filler amplifies the microscopic deformation of the rubber phase and thus reduces the onset strain amplitude of Payne effect. The nonlinear dynamic modulus can be normalized into master curves as a function of microscopic strain amplitude of rubber phase in the nanocomposites.^[20,22–27] Being different from the strain stiffening of associating networks of unentangled network strands,^[28,29] entangled linear polymers exhibit shear thinning at reptation Weissenberg number (Wi_{rep}) above 1,^[30] which has been assigned to shear-induced reduction of entanglement density,^[31] and convective constraint release effect^[32] and its incorporation with contour length fluctuation effect.^[33] However, both rubber vulcanizates and nanocomposites soften at the timescale being much shorter than that of reptation^[22,25] and efforts made to incorporate convective constraint release effect to simulate the LAOS nonlinearity^[15] do not succeed.^[8] On the contrary, the conformational perturbation and size change of Pincus blob may play a vitally important role^[34–38] and shear thinning is an indication of deviations of polymer dynamics from the classical Rouse model.^[39] The nonlinear Rouse dynamics of network strands may also account for the Payne effect of nanocomposites based on end-linking polydimethylsiloxane networks.^[16] Nevertheless, the relationship between conformational change of chains and strain softening in diverse polymeric systems needs to be studied.

The perspective of this study is aimed at proposal of a more general mechanism about the strain softening covering Payne effect. A model study is performed to investigate the strain softening in two different conditions where the filler phase remains intact or completely disassociates. This is accomplished by using styrene-isoprene-styrene (SIS) copolymers at temperatures (T) below and above glass transition temperature (T_g) of the polystyrene (PS) phase. The middle rubbery polyisoprene (PI) blocks mainly taking loop or bridge conformations are chemically interconnected by nanosized PS domains^[40,41] and the dynamics are dominated by the entangled PI blocks at $T < T_{g,PS}$. At $T > T_{g,PS}$, end fluctuation of bridging chains can happen.^[40,41] As ω decreases further, mesophase relaxation or “layer diffusion” couples with single chain relaxation,^[42] yielding an additional regime of modulus plateau well below the high- ω entanglement plateau.^[43] Shear flow of melts and solutions of block copolymers may influence the order-to-disorder transition temperature (T_{ODT}) and cause phase stability and orientation^[44,45] while the LAOS behaviors at temperatures far below T_{ODT} are less understood. In this article, the LAOS behaviors of SIS copolymers are investigated to provide insight into the Payne effect of rubber nanocomposites. For comparison with rubber vulcanizates, the PI phase is selectively crosslinked. The article is organized

as follows. The dynamics of SIS copolymers are firstly investigated *via* broadband dielectric spectra. Next, linear rheological responses are studied. Then, strain softening behaviors at temperatures below and above $T_{g,PS}$ and the domain orientation after shear are investigated. Finally, the relationships between density of elastically active network strands (EANS) and Payne effect of SIS and polyisoprene rubber (IR) vulcanizates and compounds are discussed. The results show that density of EANS is a key parameter controlling the softening in these diverse polymeric systems.

EXPERIMENTAL

Materials

Narrow molecular weight distribution SIS copolymers (polydispersity 1.02–1.03, density 0.92 g·cm⁻³) were purchased from Baling Petrochem. Co., Ltd., China. Comparative studies for different molecular architectures were conducted. The two linear copolymers (SIS_{L1} and SIS_{L2}) possess different volume fraction of PS block (ϕ_{PS}) and the star shaped copolymer (SIS_S) contains a small amount of linear diblock molecules resulting from coupling reaction. Details about weight-averaged molecular weight (M_w) and molecular composition are listed in Table 1.

Apparent molecular weights of the copolymers were determined at 298 K by gel permeation chromatography (Waters 2690, Waters Co., USA) using tetrahydrofuran as the mobile phase and PS as the standard calibration. Actual molar masses of the copolymers were measured by multi-angle laser light scattering detectors (Wyatt HELEOS, Wyatt Technol., USA) combined with a size exclusion chromatography. Determination of M_w was shown in Fig. S1 (in the electronic supplementary information, ESI). As is seen, $M_{w,PI}$ is much higher than weight-averaged entanglement molecular weight of PI ($M_{e,PI}$ =4.8 kg·mol⁻¹) and $M_{w,PS}$ is less than 2 times of weight-averaged entanglement molecular weight of PS ($M_{e,PS}$ =16.5 kg·mol⁻¹).^[46,47] Weight fraction of star shaped molecules in SIS_S was determined as 0.86 from the ratio of integral areas between Gaussian fitting peaks in gel permeation chromatography curves (Fig. S1 in ESI). It is known that one star-like molecule is composited of 2–3 linear diblock “arms”. Block fraction was determined by proton nuclear magnetic resonance spectroscopy (Fig. S2 in ESI) recorded on an Agilent 600 MHz DD2 (DirectDrive2) spectrometer (Santa Clara, USA) using tetramethylsilane as the internal standard for calibration. The copolymers were dissolved in deuterated chloroform in 0.05% concentration. M_w of the PI block is calculated from the whole chain M_w and block fraction, assuming equal M_w of PS block ends.

Liquid polyisoprene (LIR; density 0.91 g·cm⁻³, M_w =63.6

Table 1 Molecular structures of SIS.

Sample	M_w (kg·mol ⁻¹)		Molar fraction of isoprene		Volume fraction of isoprene	
	PI block	Whole chain	1,4-Structure	3,4-Structure	1,4-Structure	3,4-Structure
SIS _{L1}	136	158	0.82	0.08	0.80	0.08
SIS _{L2}	79	110	0.73	0.07	0.68	0.07
SIS _S	Linear diblock: 83	115 ^b	0.80	0.07	0.77	0.07
	Star block: ^a 249	303				

^a Fraction of star block is 0.86; ^b Estimated from ratio of peak molar masses measured by gel permeation chromatography (Fig. S1 in ESI).

kg·mol⁻¹, polydispersity 1.15) and polyisoprene rubber (IR; M_w =1480 kg·mol⁻¹, polydispersity 1.66, and *cis*-1,4 content 98.5%) were from Kuraray Co., Ltd., Japan, and Zeon Chem., Japan, respectively. Isooctane was from Shanghai Aladdin Ind. Co., Ltd., China. Carbyltetramethylene tetrakis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate) (antioxidant 1010) was delivered from Shanghai Macklin Biochem. Co., Ltd., China. Carbon black (CB; N330, primary particle size 30 nm, density 1.86 g·cm⁻³, and dibutyl phthalate absorption 1.00 cm³·g⁻¹) was from Longxing Chem., China. Dicumyl peroxide (DCP) was from Sigma-Aldrich. Stock Co. Ltd., China.

Sample Preparations

SIS containing 0.5 phr (parts per hundred rubber) antioxidant was mixed at 393 K and 40 r/min for 20 min in a torque rheometer (XSS-300, Kechuang Rubber Plastic Mechan. Equipment Co., Ltd., China). To introduce inter-molecular crosslinking structure, 1 phr or 3 phr DCP was added during the mixing process. Chemical crosslinking from DCP, physical crosslinking from micro-domain and trapped entanglements between crosslinking sites can contribute to effective network density (ν_c ; Table 2) determined according to Flory-Rehner equation (as described in ESI) by selectively swelling the PI phase using isooctane.^[48] Chemical crosslinking of the PI phase by DCP yields nonideally crosslinked network by coupling of macromolecular radicals on the one hand and yields a certain amount of sol fraction by terminating of radicals on the other hand.^[22] The apparent M_w and dispersity were determined by tetrahydrofuran extraction (Table 3). The CB filled IR nanocomposites and the DCP-containing IR compounds were mixed at 373 K and 40 rpm in the torque rheometer. Volume fraction of CB (ϕ_{CB}) in the IR compounds and crosslinking density of IR vulcanizates were controlled by adjusting CB and DCP dosages, respectively.^[8]

The SIS and IR compounds with DCP were compressed into sheets of 1.5 mm in thickness under 14.5 MPa at 413 K for 40 min. The sheets were cut into discs of 25 mm in diameter for rheological tests. Discs of 0.3 mm in thickness and 20 mm in diameter were prepared for investigation of dielectric behaviors.

Measurements

A strain-controlled rheometer (ARES-G2, TA Instrument, USA) equipped with a serrated surface plate clamp was used to

perform T ramp (from 303 K to 510 K) at 1% strain amplitude (γ_0), 1 rad·s⁻¹ frequency (ω) and 3 K·min⁻¹ ramp rate to identify $T_{g,PS}$ and T_{ODT} . The ω -sweeps at γ_0 =0.5% were performed to characterize linear rheological behaviors, and the γ_0 -sweeps were carried out to study the strain softening behavior at T =343 K and 393 K. In order to access reliable mechanical data under every γ_0 , the pre-delayed 20 cycles were abandoned and the subsequent 20 cycles were sampled. Raw stress and strain data recorded during LAOS tests were analyzed with FT-filtering technique to quantify the nonlinear responses.

A Novocontrol Alpha broadband dielectric spectrometer (GmbH Concept 40, Novocontrol Technol., Germany) was used to record complex dielectric permittivity (ϵ^*) from frequency (f) 10⁷ Hz to 10⁻¹ Hz at T between 223 K and 473 K.

Small angle X-ray scattering (SAXS) experiments were performed on a SAXS/WAXS system (Xenocs, France) equipped with a semiconductor detector (Pilatus 100 K, Dectris, Swiss) attached to a Cu K α source (wavelength λ =0.154 nm) generated at 50 kV voltage and 0.6 mA current. The sample to detector (pixel size 172 μ m) distance was 1375 mm. For discs experiencing LAOS tests, the X-ray beam was irradiated perpendicular to the shear plane on the half of radius from the outer edge. The 2D scattering patterns were analyzed by using a FIT2D software to obtain integrated intensities (I) with respect to scattering vector $q=4\pi\sin\theta/\lambda$ and azimuthal angle (ϕ). Here 2θ is scattering angle.

Dispersity of PS domains in SIS was characterized using transmission electron microscopy (TEM, Hitachi HT7700, Japan) at 120 kV accelerating voltage. Samples cut into thin sections with ultramicrotome (EMUC7, Leica, Germany) were stained by OsO₄ vapor.

RESULTS AND DISCUSSION

Molecular Dynamics

For the SIS copolymers, $T_{g,PS}$ is determined as 380 K^[47] according to the decay of storage modulus (G') and peaking of loss modulus (G'') during the T -sweep (Fig. S3 in ESI).^[49,50] At $T_{g,PS}<T<510$ K, only the star-shaped copolymer SIS₅ containing some diblock molecules exhibits a distinct G' decrease at 486 K corresponding to order-to-disorder transition.^[51] The rheological responses reported hereafter are at temperatures well below T_{ODT} .

Dipole moment of type-A PI block can be decomposed into components parallel and perpendicular to the chain contour, referring as to the normal and segmental modes, respectively.^[52] Fig. 1 shows master curves of dielectric loss (ϵ'') versus normalized frequency ($a_T f$) at reference temperatures (T_{ref}) below and above $T_{g,PS}$ and horizontal shifting factors (a_T) versus T . Below and above $T_{g,PS}$, a_T can be respectively described by Vogel-Fulcher-Tamman (VFT) equation:^[53–55]

$$\log a_T = B \left(\frac{1}{T - T_0} - \frac{1}{T_{ref} - T_0} \right) \quad (1)$$

and Arrhenius relation:

$$\log a_T \sim \frac{E}{T} \quad (2)$$

where B is activation parameter, T_0 is Vogel temperature and E is apparent activation energy. At $T<T_{g,PS}$, both B and T_0 are insensitive to ν_c (Table S1 in ESI). However, the segmental friction of the PI block is influenced by the molecular

Table 2 ν_c in mol·m⁻³ for uncrosslinked or selectively crosslinked SIS.

DCP dosage (phr)	0	1	3
SIS _{L1}	2.58	4.64	136.51
SIS _{L2}	2.97	22.51	114.72
SIS ₅	2.49	8.47	75.77

Table 3 Apparent M_w , polydispersity and content of sol fraction extracted from selectively crosslinked SIS.

DCP dosage (phr)	Content ^a (%)		M_w (kg·mol ⁻¹)		Polydispersity	
	1	3	1	3	1	3
SIS _{L1}	14	3	85	16	2.31	1.36
SIS _{L2}	10	7	79	21	1.98	1.51
SIS ₅	12	5	48	18	1.48	1.50

^a Weight fraction with respect to the SIS sample.

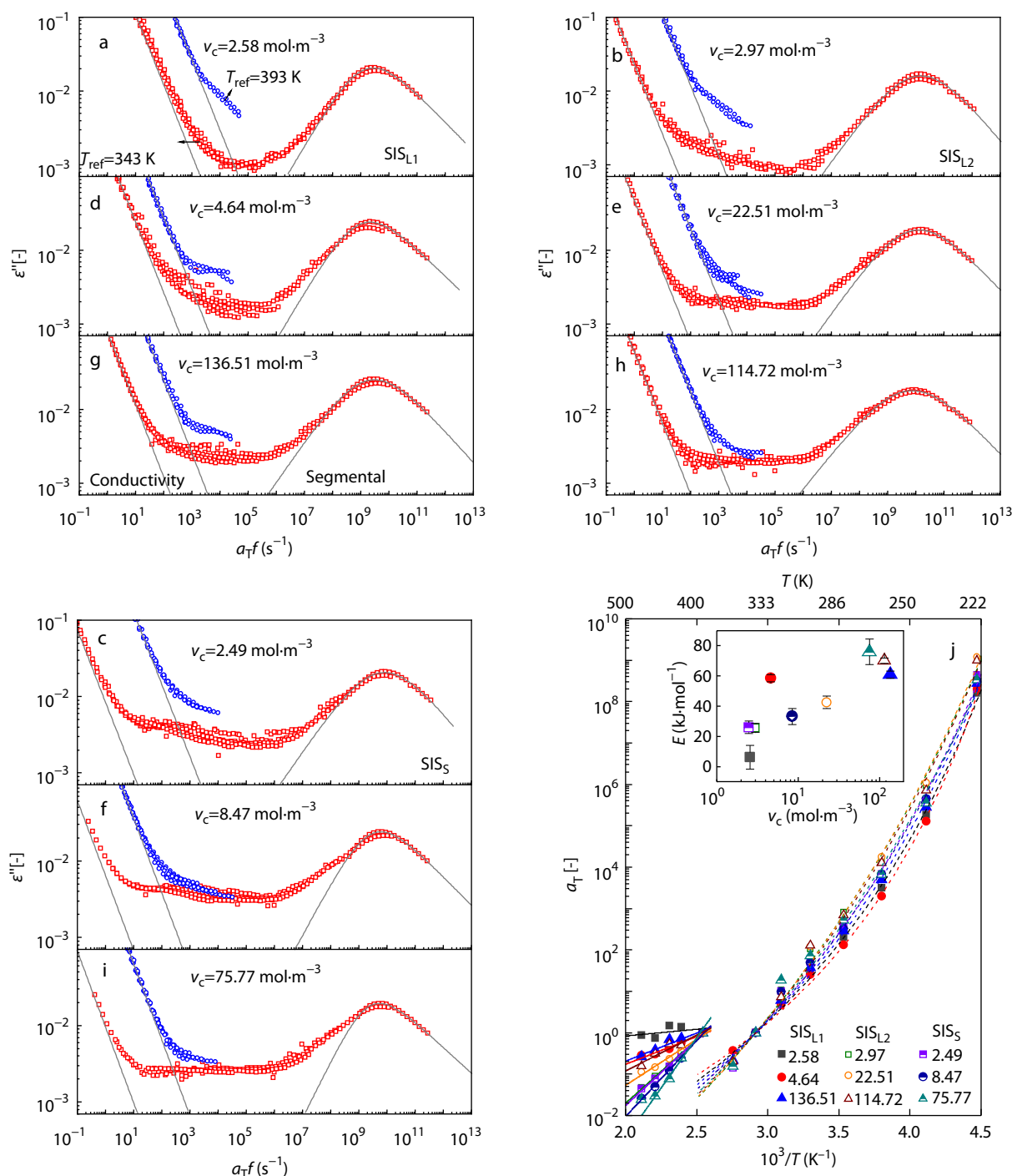


Fig. 1 Master curves of ϵ'' and horizontal shifting factor a_T for SIS of varying v_c . ϵ'' as a function of normalized frequency ($a_T f$) for SIS_{L1} (a, d, and g), SIS_{L2} (b, e, and h) and SIS_S (c, f, and i) and a_T as a function of reciprocal temperature ($1/T$); j). In (a-i), the master curves at $T_{\text{ref}} = 343$ K and $T_{\text{ref}} = 393$ K are constructed by horizontally shifting the data measured at temperatures from 223 K to 363 K and those from 393 K to 473 K, respectively, and the curves at high- and low-frequencies are fitted from HN equation and power-law electrical conductivity, respectively. In (j), the solid lines and dash curves are drawn according to Arrhenius and VFT relations, respectively, and the inset shows apparent activation energy E at $T > T_{g,PS}$ as a function of v_c .

architecture so that B decreases and T_0 increases in the order of SIS_{L2}, SIS_S and SIS_{L1}. At $T > T_{g,PS}$, the PI blocks can not only fluctuate but also jump between the softened PS domains^[56] while E is less sensitive to the molecular architecture. On the other hand, E increases significantly with increasing v_c , revealing

that the formation of network in the PI phase efficiently restricts the molecular diffusion in comparison with the linear chains.^[57]

In the dielectric spectra, the ϵ'' peak around 10^{10} s⁻¹ at 343 K can be ascribed to segmental relaxation of PI block.^[57] Single mode Havriliak-Negami (HN) equation:^[58]

$$\varepsilon^* - \varepsilon_\infty = \frac{\Delta\varepsilon}{[1 + (i\omega\tau_{\text{HN}})^a]^\beta} \quad (3)$$

and power-law electrical conductivity:

$$\varepsilon'' = \frac{\sigma_0}{\varepsilon_0 f^s} \quad (4)$$

are used to extract contributions of segmental relaxation and electrical conductivity in the high- and low- f regions, respectively. Here $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ is relaxation strength, ε_0 is permittivity of free space, ε_∞ is unrelaxed permittivity, τ_{HN} is characteristic relaxation time, a is asymmetry parameter, β is broadness parameter, and σ_0 and s are fitting parameters. The fitted τ_{HN} values vary between 1.31×10^{-11} to 1.63×10^{-10} s for SIS of varying v_c (Table S2 in ESI), revealing that, the segmental relaxation of the PI block is somewhat sensitive to dangling chains generated by crosslinking reaction.^[59]

At $T < T_{g,\text{PS}}$, no ε'' peaks of normal mode can be seen in between the segmental mode and the electrical conduction process (Fig. 1) because the end fluctuation of PI blocks at the quiescent state is restricted by the rigid PS domains.^[40,41] At $T > T_{g,\text{PS}}$, the end-to-end fluctuation of the PI block slightly changes the temperature dependence of a_T . The segmental dipole motion of type-B PS blocks has minor contributions to the low- f relaxation.^[41] Furthermore, the presence of PS domains and the selective crosslinking of the PI phase significantly influence the interval between the segmental mode and electrical conduction process. The broadening reflecting dynamics coupling of submolecules^[52,60] in tube theory^[61] is more marked in the star-like SISs and it becomes heavy as v_c increases.

Linear Rheological Behaviors

Fig. 2 shows master curves of linear rheological responses for uncrosslinked SIS at $T_{\text{ref}}=343$ K created according to time-

temperature superposition principle. The vertical shifting factor (b_T) varies about 1 due to less changes of density and morphology with T and the horizontal shifting factor (a_T) follows the VFT relation. In the T range covering $T_{g,\text{PS}}$ and being far below T_{ODT} , there should be little morphological change^[42,62] even though the PS domains are glassy at $T < T_{g,\text{PS}}$ and rubbery at $T_{g,\text{PS}} < T < T_{\text{ODT}}$. According to product of mixing parameter χ and polymerization degree N (for SIS_S, N is specified to the diblock arm), $\chi N=111$, 73 and 76 for SIS_{L1}, SIS_{L2} and SIS_S, respectively, all the copolymers are in the strong segregation regime even at the highest testing T (453 K).^[62] Here χ is estimated via an empirical relation $\chi=33/T - 0.0228$ ^[43,63] for diblock and triblock copolymers of PS and PI. The copolymers form nanosized cylinder morphology being not perfectly ordered (Fig. S4 in ESI). The time-temperature superposition principle is applicable in the T range with stable morphology and a_T being mainly related to relaxation of the PI phase is slightly influenced by the low- ϕ_{PS} PS phase (Table S3 in ESI). Among the fitted VFT parameters (Table S3 in ESI), B decreases in the order of SIS_{L2}, SIS_S and SIS_{L1}, being the same as the results of dielectric behaviors.

The master curves of uncrosslinked SIS copolymers at $T_{\text{ref}}=343$ K can be divided into different relaxation regimes. The moduli at high ω are dominated by the dynamics of entangled PI blocks and are influenced by ϕ_{PS} . In the intermediate ω regime corresponding to $T > T_{g,\text{PS}}$, the PS blocks relax and the PI blocks fluctuate, yielding parallel behaviors of G' and G'' scaling like $\omega^{0.5}$ and peaking of $\tan\delta$. This scaling being common for block copolymers of diverse molecular architecture, block number and microdomain morphology^[42,43,64,65] arises from mesophase relaxation coupled with the PI block relaxation.^[42] As ω decreases further, moduli of SIS_{L1} decay continually^[42] while an additional G' plateau well below the entanglement plateau^[43] appears in SIS_{L2} and SIS_S. The low- ω plateau seems strongly dependent

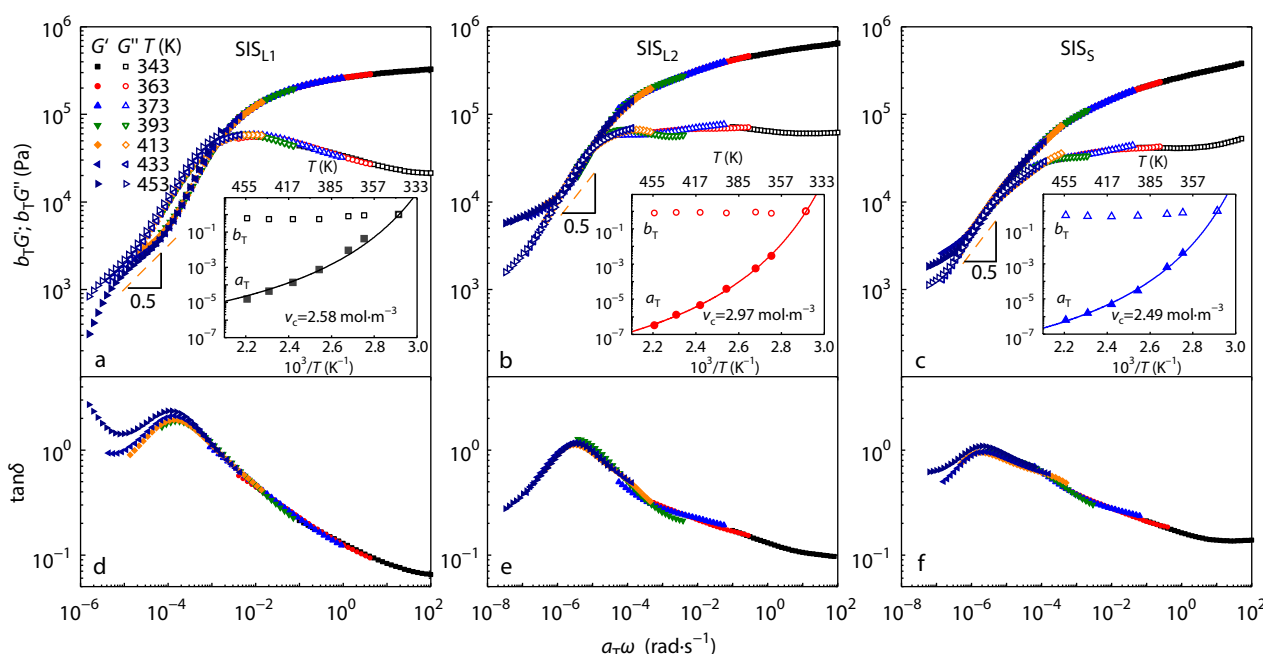


Fig. 2 Master curves of linear rheological responses of uncrosslinked SIS copolymers at $T_{\text{ref}}=343$ K. The data measured at temperatures between 343 K and 453 K are used to create master curves of G' (a, b, and c: solid symbols), G'' (a, b, and c: hollow symbols) and $\tan\delta$ (d, e, and f). Insets show vertical (b_T , open symbols) and horizontal shifting factors (a_T , solid symbols) and the predicted VFT relation (solid curves).

on ϕ_{PS} and the solid-like behavior ($G' > G''$) in SIS_{L2} with $\phi_{PS}=0.25$ is more obvious than that in SIS_S with $\phi_{PS}=0.16$. The additional G' plateau at low- ω regime may come from the disentanglement of PI blocks.^[66,67]

Linear rheological behaviors of the selectively crosslinked SIS are investigated (Fig. S5 in ESI). The chemical crosslinking rarely changes domain morphology (as confirmed by SAXS discussed later and TEM images shown in Figs. S6 and S7 in ESI). At 343 K, G' and G'' decay slightly and $\tan\delta$ increases with decreasing ω , reflecting Rouse-like dynamics of EANS. The weak ω -dependent linear rheological response is related to the branched PI chains^[68] and a small content of sol fraction^[22] generated by random chemical crosslinking. The sol chains with $M_w \gg M_{e,PI}$ may entangle with the PI blocks or associate with the PS blocks, behaving like EANS. At 393 K where the PS blocks disassociate from their domains and become dangling chains, the sensitivities of G' and G'' to ω become significant and $\tan\delta$ peaks in the intermediate ω region. The relaxation time of the dangling chain decreases when its length decreases with increasing v_c ^[69] causing shift of the $\tan\delta$ peak to high ω at 393 K.

Nonlinear Rheological Behaviors

LAOS behaviors of SIS at 10 rad·s⁻¹ under 343 and 393 K are

investigated using FT-filtering technique. Under shear strain $\gamma(t) = \gamma_0 \sin(\omega t)$, shear stress takes the form

$$\sigma(t; \omega, \gamma_0) = \gamma_0 \sum_{n: \text{odd}} G_n^* \sin(n\omega t + \delta_n) \quad (5)$$

where $G_n^* = (G_n'^2 + G_n''^2)^{1/2}$ and $\delta_n = \tan^{-1}(G_n''/G_n')$ are the n^{th} -order complex modulus and phase angle, respectively. Fig. 3 displays the first-order rheological parameters G_1^* and $\tan\delta_1$ as a function of γ_0 under cyclic LAOS tests. At small γ_0 , G_1^* reduces to linear modulus G_0^* with constant value. As γ_0 increases beyond a critical strain amplitude γ_c , SIS exhibits strain softening characterized by marked G_1^* decay and $\tan\delta_1$ increment. At 343 K where the PS domains survive, the cyclic LAOS tests have little influence on G_0^* except for the occurrence of weak hysteresis in the nonlinear region. The $\tan\delta_1$ increment in the nonlinear region can be ascribed to the improved viscous nonlinearity,^[8] which, however, almost overlaps under different LAOS periods. The reversible strain softening at 343 K indicates that the elastically active network does not damage during cyclic LAOS deformation. At 393 K where the PS domains become rubbery, γ_c obviously elevates in comparison with that at 343 K, which is similar with the resin filled rubber compounds at temperatures above T_g of resin.^[70] Above $T_{g,PS}$, the cyclic LAOS causes successive decay of G_0^* accompanied by increment of γ_c .

According to Eq. (5), the linear response reduces to the

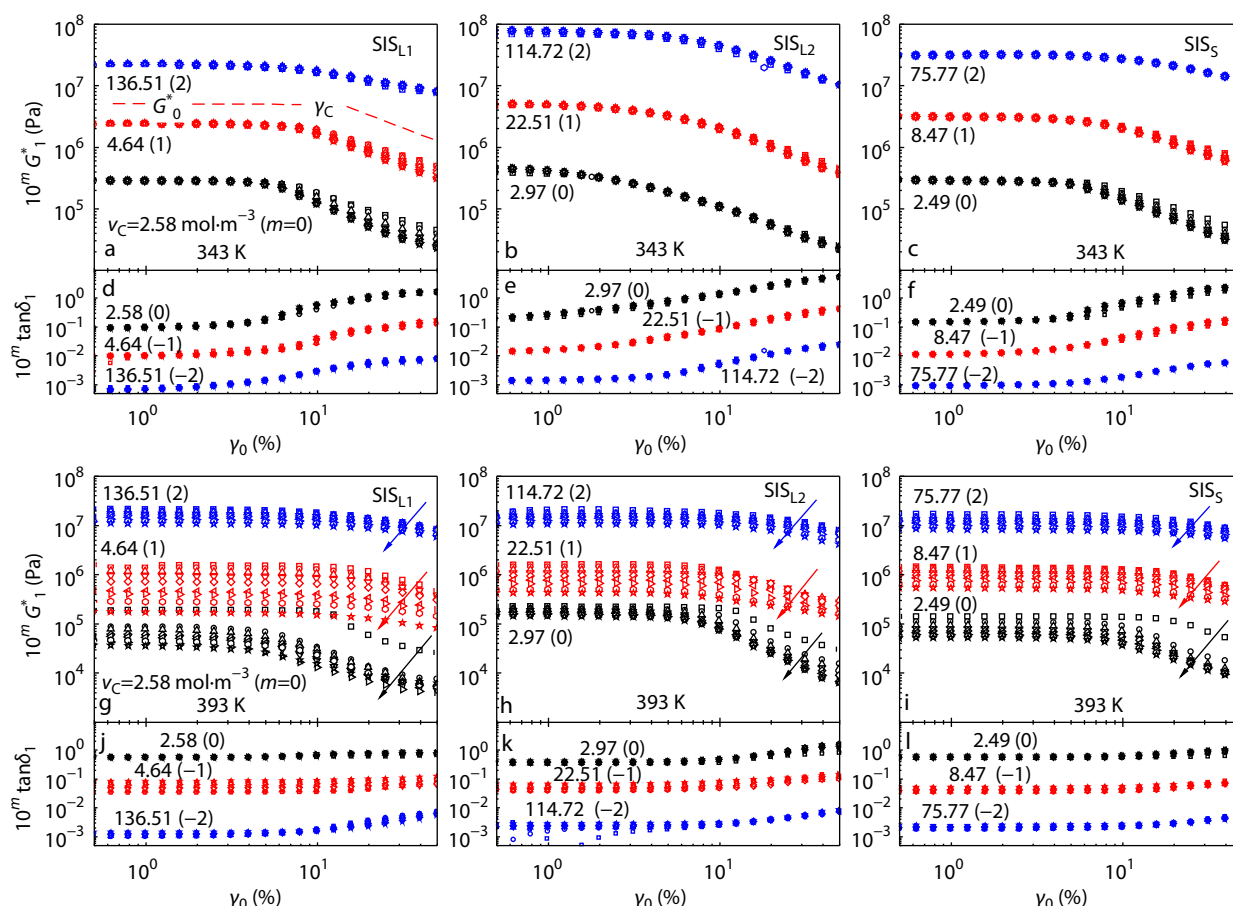


Fig. 3 Nonlinear rheological response of SIS at 10 rad·s⁻¹ at 343 and 393 K. G_1^* and $\tan\delta_1$ for SIS_{L1} (a, d, g, j), SIS_{L2} (b, e, h, k) and SIS_S (c, f, i, l) of varying v_c indicated. Each symbol represents one cyclic test cycle. To distinguish the data, they are vertically shifted by a factor 10^m . The arrows show the developing trends of G_1^* as LAOS period increases. In (a), dashed lines indicate the determination of linear modulus (G_0^*) and onset strain of softening (γ_c).

first-order harmonic while the nonlinearity is usually accompanied by pronounced higher-order harmonics. In order to quantify the LAOS nonlinearity, relative harmonic intensity ratio $I_{3/1} \equiv G_3^*/G_1^*$ is determined^[71] (Fig. S8 in ESI). $I_{3/1}$ fluctuates around 0 in the linear region but it increases markedly as soon as strain softening happens. The measured γ_c is approximately correlated with $I_{3/1}=0.05$. It can be found that $I_{3/1}$ and γ_c at 343 K show less deviation between different LAOS periods in comparison with those measured at 393 K, being in accordance with the strain softening results (Fig. 3). Fig. 4 shows schematic diagrams of microstructural variations of SIS at 343 K and 393 K. Below $T_{g,PS}$, the PI blocks are restricted by the PS domains, resulting in the reversible LAOS behaviors (Figs. 3a–3c). At 393 K, the LAOS test ω (10 rad·s⁻¹) corresponding to a timescale being far below that of the PI block disentangle-

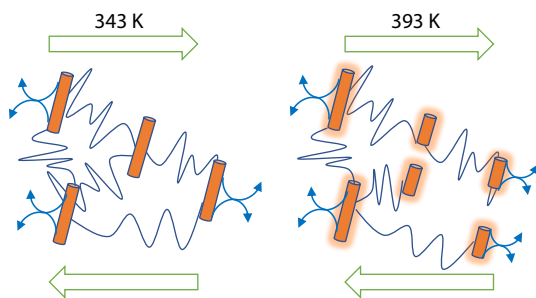


Fig. 4 Schematic diagrams showing microstructural variations of SIS under LAOS at 343 K and 393 K. The PS microdomains remain intact at 343 K and dissociate or break at 393 K.

ment (Fig. 3), the dissociation and breakdown the PS blocks cause reduction of the number density of EANS and successive decay of G_0^* (Figs. 3g–3i). LAOS tests influence absolute complex modulus G^* as a function of ω for the SIS samples (Fig. S9 in ESI). At 343 K, the cyclic deformation causes a very slight reduction in G^* . At 393 K, the cyclic LAOS test significantly lowers G^* , which is an indication of the deformation and fragmentation of PS domains being responsible for the irreversible softening (Fig. 3). The influences of LAOS deformation on the reversibility of rheological responses are examined via sequential tests after heating the samples to 343 K and 393 K and cooling to 343 K (Fig. S10 in ESI). The LAOS action at 393 K does not influence linear rheology but improves γ_c for the samples at 343 K, except for SIS_{L2} ($\phi_{PS}=0.25$) with $v_c=2.97$ and 22.51 mol·m⁻³. In the latter, the shear actions at 393 K greatly improve G^* and G_1^* in the linearity regime at 343 K, which may be inferred as fragmentation of some PS domains and the resultant increase of density of EANS induced by the high-temperature LAOS action. It means that ϕ_{PS} and v_c are important for the recovery of PS domains experiencing damage during high-temperature LAOS test.

While alignment happening on the timescale of LAOS period may not significantly influence shear modulus,^[72] slippage of domain lattice on the timescale of mesophase relaxation may induce viscoplasticity under LAOS.^[73] The bridged EANS can hinder the shear orientation and relative slide of microdomains.^[74] SAXS profiles of $I(q)$ and $I(\phi)$ (Fig. 5 and Fig. S11 in ESI) are used to analyze the morphology and orientation of

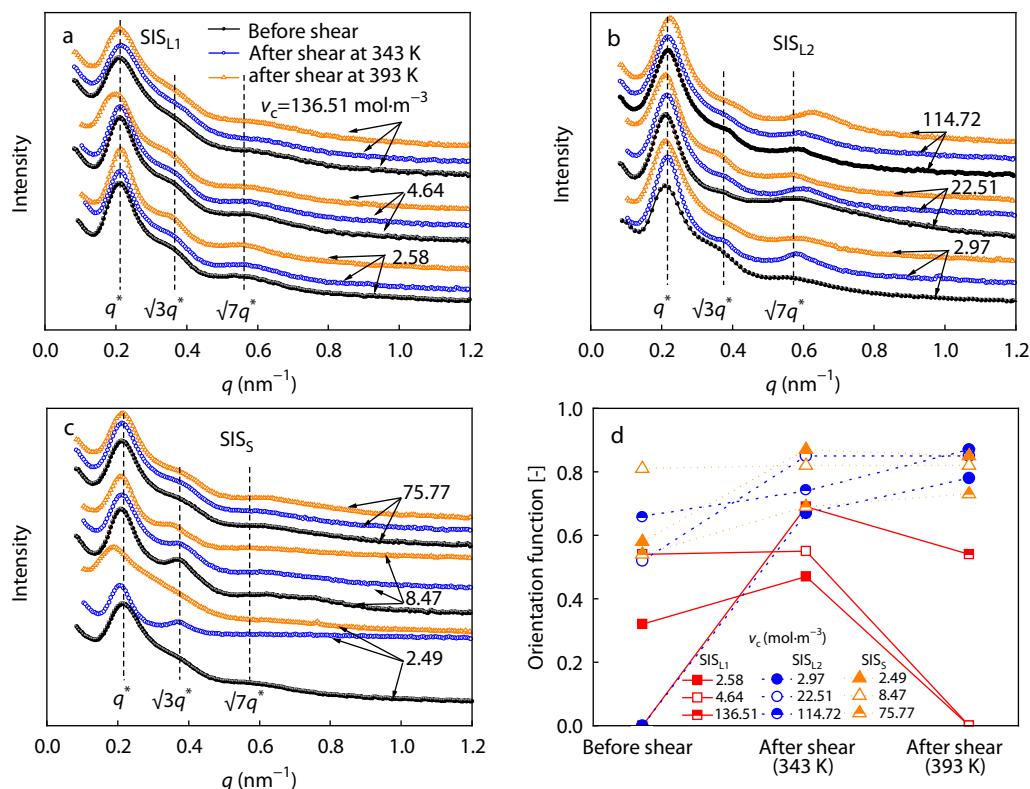


Fig. 5 Influence of cyclic LAOS deformation on SAXS profile and orientation function for SIS. The q dependence of intensity (a–c) and orientation function (d) for SIS_{L1}, SIS_{L2} and SIS_S before and after cyclic LAOS deformation at 343 K and 393 K. The vertical dash lines in (a–c) mark the locations of classical reflections at q^* , $\sqrt{3}q^*$ and $\sqrt{7}q^*$.

the PS domains in the as-prepared samples and in those experienced LAOS tests and quenched to room temperature.

As shown in Figs. 5(a)–5(c), $I(q)$ exhibits the classical high-order reflections at wavevectors of q^* , $\sqrt{3}q^*$ and $\sqrt{7}q^*$, indicating hexagonally packed cylindric morphology^[75] that is rarely influenced by chemical crosslinking and LAOS action. The cylindric morphology is not perfectly perpendicular to the sample sections (Figs. S4, S6 and S7 in ESI). Here q^* is first-order maximum scattering wavevector. Long-range order (L_0) of the PS domain estimated by Bragg's law $L_0 = 2\pi/q^*$ is about 30 nm, 28 nm and 28 nm for SIS_{L1}, SIS_{L2} and SIS_S, respectively, being in line with that estimated in TEM images (Fig. S4 in ESI). The LAOS test causes some decrease in intensity of the $\sqrt{7}q^*$ reflection due to shear induced misalignment of domain lattice planes.^[76] From the 2D SAXS patterns of the shear plane (Fig. S11 in ESI), the SIS samples before and after shear display anisotropy characterized by orientation function quantified by $1-H/180$. Here H is half-width of the peak of integrated intensity profile as a function ϕ . The as-prepared samples exhibit anisotropy (Fig. 5d) generated in the compression shaping during preparation. The LAOS deformation improves the anisotropy except for the uncrosslinked and slightly crosslinked SIS_{L1} at 393 K where the relaxation somewhat randomizes the materials. It is clear that the strain softening, that is reversible at 343 K and is irreversible at 393 K, is independent of domain orientation. On the other hand, it mainly reflects nonlinear rheology of the rubbery PI phase at 343 K and is in principle influenced by the softened PS blocks at 393 K.

Unique Mechanism on Strain Softening

The Payne effect in highly filled rubber nanocomposites is once ascribed to destruction of rubber-filler interaction^[12,77] or chain disentanglement at the interface/bulk phase.^[14,15] Such mechanisms could not explain the same phenomenon in SIS whether if its rubbery PI phase is selectively crosslinked or not. The rheological behaviors of SIS are compared with those of CB filled IR nanocomposites and IR vulcanizates (Figs. 6 and 7).

In order to calculate the entanglement and relaxation parameters, rheology of narrow molecular weight distribution LIR is also studied. The linear rheology of LIR at 253 K can be described well by Likhtman and McLeish theory^[78] with constraint release intensity parameter 0.1, Rouse time $\tau_e = 0.7$ ms, reptation time $\tau_{rep} = 0.3$ s and entanglement plateau modulus $G_e = 0.27$ MPa, respectively. Considering that G_e is independent of T and polydispersity^[79] for entangled polymers with the same chemical structure, the density of elastically active entanglement network strands of LIR and IR gums are estimated as 160.4 and 121.9 mol·m⁻³, respectively.

In Fig. 6(a), G' and G'' of the nanocomposites are vertically shifted to form a master curve at the high- ω side and the reciprocal vertical shifting factor ($1/b$) is indicative of hydrodynamic reinforcement effect^[80,81] being extensively studied. In the compounds, CB nanoparticles are mostly dispersed in the form of aggregates (Fig. S12 in ESI) and the hydrodynamic effect is highly dependent on the fractal structure of the aggregates.^[80,81] Taking account of the far-field interaction between fillers, a general form by Chen *et al.*^[82] is used to describe the high- ω modulus ratio $1/b$ as:

$$1/b = 1 + 2.5\varphi_a + (2.5\varphi_a)^2 + o(\varphi_a^3) \quad (6)$$

where $\varphi_a = \varphi_{CB}(a_a/a)^{3-D}$ is effective volume fraction of CB aggregates, D is fractal index, and a and a_a are radii of the nanoparticle and aggregate, respectively. According to TEM images (Fig. S12 in ESI), a_a is around 62 nm being two times of the size of primitive CB nanoparticle. The CB aggregate belongs to the category of diffusion-limited cluster aggregation with $D=1.8$.^[81,82] Eq. (6) approximates $1/b$ well (Fig. 6d), indicating that the high- ω reinforcement mainly comes from the hydrodynamic effect induced by CB fractals. Although bridging chains^[83] or confined diffusion of nanoparticles^[84] may retard the relaxation and lower $\tan\delta$ in the low- ω regime, the relaxation in high- ω regime is dominated by the rubber matrix, as shown in Fig. 6(b). In the nanocomposites, the segmental and chain dynamics are decoupled.^[85] According to empirical relations^[47] $G_e = \exp(-T/635)kT/200p_a^3$ and $a_{tube} = 14.0\exp(T/1270)p$, entanglement tube diameter a_{tube} of the IR gum at 333 K is estimated as 6.7 nm, being much smaller than the size of CB. Here k is Boltzmann constant and p_a is packing length. It is seen that the diffusion of CB nanoparticles is severely suppressed^[86] and that CB rarely influences the entanglement of rubber matrix. Thus, ν_e of nanocomposites is taken the same as entanglement density of the IR gum.

Fig. 7 shows strain softening behaviors of IR vulcanizates ($\nu_e = 45$ mol·m⁻³), IR compounds and LIR. Although the LAOS curves of IR vulcanizates are close to each other at 308 K and 333 K, $I_{3/1}$ shows some discrepancy in the nonlinear regime, which may come from variations of elastic and viscous nonlinearities.^[8] For LIR at the two frequencies for LAOS test (1 and 30 rad·s⁻¹) correspond to Weissenberg number $Wi_{rep} \equiv \omega\tau_{rep}$ being lower and higher than 1, respectively, strain softening occurs without exception and it is more marked at higher frequency. In the IR compounds, the filler can modify the strain field nearby by introducing strain and stress amplification effects^[23,87] that enhance the softening and nonlinearity. However, the conventional viewpoint that the Payne effect of nanocomposites is activated by the breakdown of filler agglomerate or network is not pertinent^[16] because it could not explain the softening of the unfilled linear LIR melts and the unfilled IR vulcanizates (Fig. 7). In fact, the softening of polymers, either crosslinked or not,^[16,20–22,25] and either filled or not,^[16,20,22–27] is approved to be exceedingly common.

According to linear rheological responses (Fig. 2) of SIS, the rheology is dominated by dynamics of entangled PI blocks at $T < T_{g,PS}$ while the relaxation of PS blocks followed by PI blocks fluctuation affects modulus at $T > T_{g,PS}$. The strain softening at $\omega = 10$ rad·s⁻¹ and $T = 393$ K (Fig. 3) occurs at timescale being much shorter than τ_{rep} . For SIS at $T = 343$ K and IR nanocomposites at $T = 333$ K where the ω of LAOS runs ($\omega = 10$ and 1 rad·s⁻¹) is higher than that of the $G'-G''$ crossover in the linear rheology (Fig. 2, Fig. S5 in ESI and Fig. 6), the softening is invariably observed. The softening of LIR even occurs at timescales being both shorter and longer than τ_{rep} . It means that reptation of chains and specially the dissociation of PS domains in SIS does not necessarily cause the softening. In another word, the occurrence of softening does not involve molecular movement on the time scale of τ_{rep} . Although shear thinning initiated near $Wi_{rep} = 1$ ^[30] in steady flow of entangled chains has been ascribed to partial disentanglement,^[31] con-

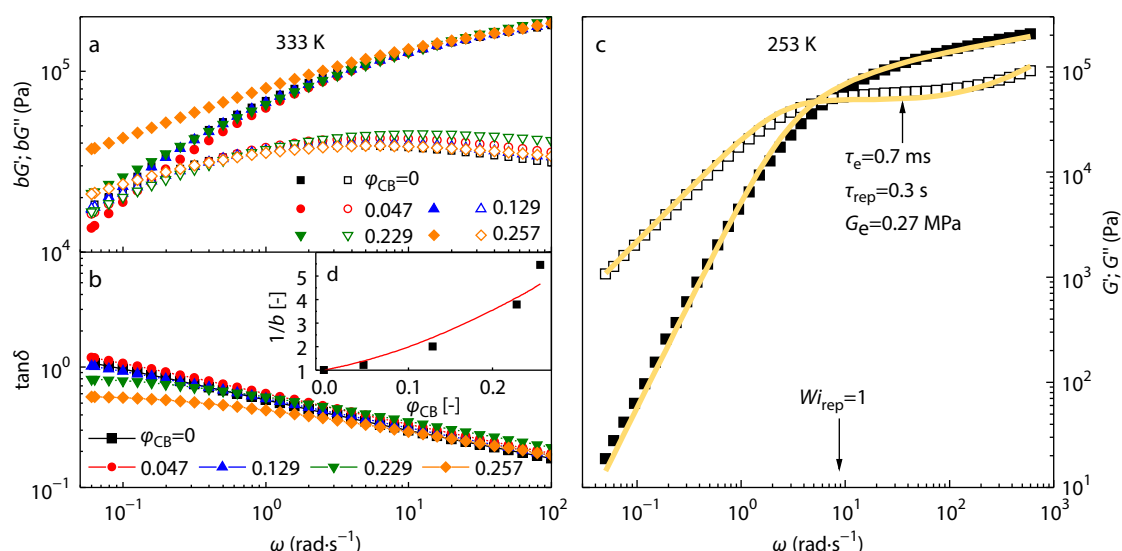


Fig. 6 Linear rheological responses for CB filled IR nanocomposites and LIR. Normalized G' (solid symbols in a) and G'' (hollow symbols in a) and $\tan\delta$ (b) for the nanocomposites with different ϕ_{CB} , and G' (solid symbols in c) and G'' (hollow symbols in c) for LIR as a function of ω . The reciprocal shifting factor ($1/b$) for IR nanocomposites is displayed in (d). The curves in (c) are drawn according to Likhtman-McLeish model with parameters indicated [78] and that in (d) is drawn according to Eq. (6).

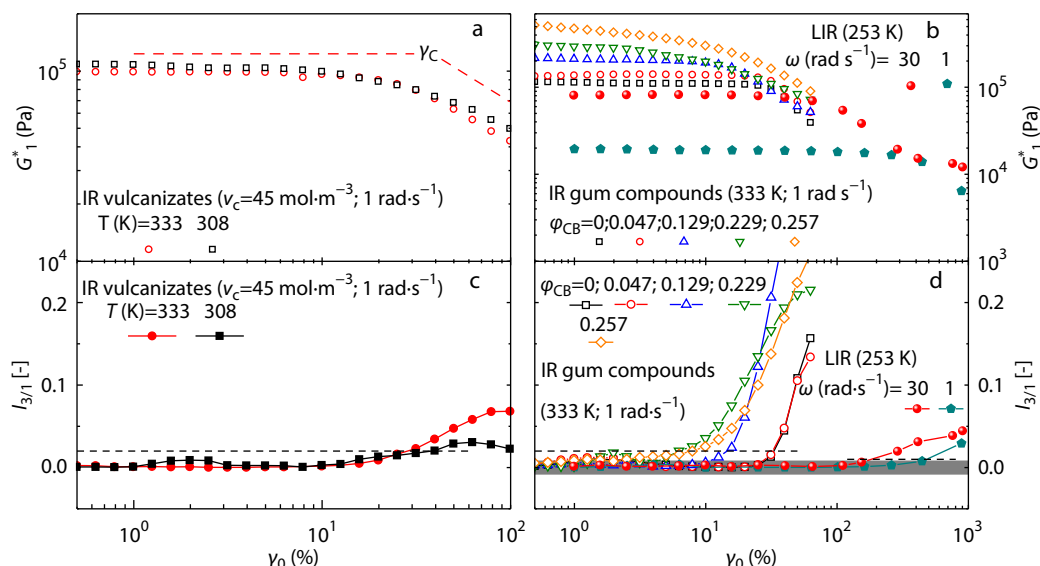


Fig. 7 Nonlinear rheological responses for IR vulcanizate, CB filled IR compounds and LIR. G^* (a, b) and $I_{3/1}$ (c, d) as function of γ_0 for IR vulcanizate (a, c), IR compounds and LIR (b, d). The intersection of two straight lines in (a) denote the determination of γ_C for IR vulcanizate, the method being applicable for CB filled IR compounds and LIR. The determined γ_C values correspond to $I_{3/1}=0.02$ for IR vulcanizate and CB filled IR compounds and $I_{3/1}=0.01$ for LIR, as indicated by dashed lines in (c) and (d).

vective constraint release^[32] and contour length fluctuation effects,^[33] these mechanisms fail for SIS melts, LIR gum and IR vulcanizates and compounds. On the other hand, the softening should occur at the timescale of intrinsic Rouse relaxation of EANS considering that both unentangled^[34–38] and entangled chains^[39] with finite extensibility^[35–37] and uncrossability^[88,89] undergo shear thinning due to deviation of Pincus blobs from Gaussian conformation.^[90]

The contribution of conformational change to strain softening of rubbery materials under LAOS is considered. The conformation of EANS is assumed to deviate from Gaussian shape when the end-to-end distance R_0 becomes compar-

able with its original size bNp , where b and N are size and number of monomer of network strands, respectively. According to free energy $F = kT[R_0/(bNp)]^{1/(1-p)}$, the force f_0 for stretching a network strand from bNp to R_0 is

$$f_0 \approx \frac{kT}{(1-p)bNp} \left(\frac{R_0}{bNp} \right)^{p/(1-p)} \quad (7)$$

Strain softening would occur when f_0 reaches a critical value where $R_0 \approx bNp$. The critical stress macroscopically applied on the rubbery materials ($G^*_0\gamma_C$) would equal to the microscopic critical stress of the deforming rubber phase (the matrix in nanocomposites and the PI phase in SIS) when affine deformation is fulfilled.^[91,92] Thus, a simple relation can

be obtained

$$\frac{G^*_{0}v_c}{v_cRT} \sim v_c^{p-1} \quad (8)$$

Fig. 8 shows $G^*_{0}v_c/(v_cRT)$ versus v_c for SIS and several rubber gum, compounds and vulcanizates. The data collected from various polymeric systems tested at various frequencies are somewhat scattered while Eq. (8) with $p=0.5$ describes the general variation trend, suggesting the onset of strain softening is closely related to conformational change of EANS. The validation of Eq. (8) for SIS copolymers and their selectively crosslinked products, for IR and butadiene rubber vulcanizates and LIR tested at the timescales being shorter and longer than τ_{rep} , for butadiene rubber vulcanizates with or without sol fraction, and for CB filled IR compounds suggests that the strain softening is related to the length scale of EANS. Furthermore, the softening is nearly independent of domain orientation in SIS and is not related to the irreversible breakdown-reformation of filler aggregates in the compounds.^[8,10,20–27]

The (selectively crosslinked) SIS copolymers differ from the rubber gums and nanocomposites in structure while the onset of strain softening in these materials are similar. In the copolymers, the PI blocks are chemically linked to the PS blocks and the chains and the PI-PS linkages do not damage under LAOS. Furthermore, the PS domain are much softer than nanoparticles. Under LAOS, the hard PS domains below $T_{g,PS}$ re-

main intact while pulling out of the PS blocks above $T_{g,PS}$ causes deformation and fragmentation of the rubbery PS domains (Fig. 3, Fig. S9 in ESI), the latter resembling the breakdown of filler aggregates and the desorption of chains from the surface of filler aggregates in rubber nanocomposites. However, at temperatures both below and above $T_{g,PS}$, the onset of strain softening of SIS is closely related to conformational change of EANS (Fig. 8) rather than the fragmentation of the rubbery PS domains caused by cyclic shear. Some local events like chain slipping in entangled polymer melts (matrix in the compounds) and nonideally crosslinked vulcanizates, misalignment of domain lattice planes in the SIS copolymers, and breakdown of filler aggregates in the compounds may cause nonaffine deformation that contributes only marginally to the major mechanism of softening rooted in the intrinsic Rouse dynamics^[16,34–39,88–90] of EANS. It is suggested that these diversified polymer systems with v_c spanning two orders of magnitude may demonstrate strain softening due to conformational changes on the scale of Rouse dynamics rather than the nonaffine deformation of the deforming units. Such mechanism could be connected to the shear thinning of both unentangled and entangled polymer melts on the one hand and could be adopted to explain the soften in low-defect polymeric systems like end-linking polydimethylsiloxane networks and their nanocomposites and SIS at $T < T_{g,PS}$.

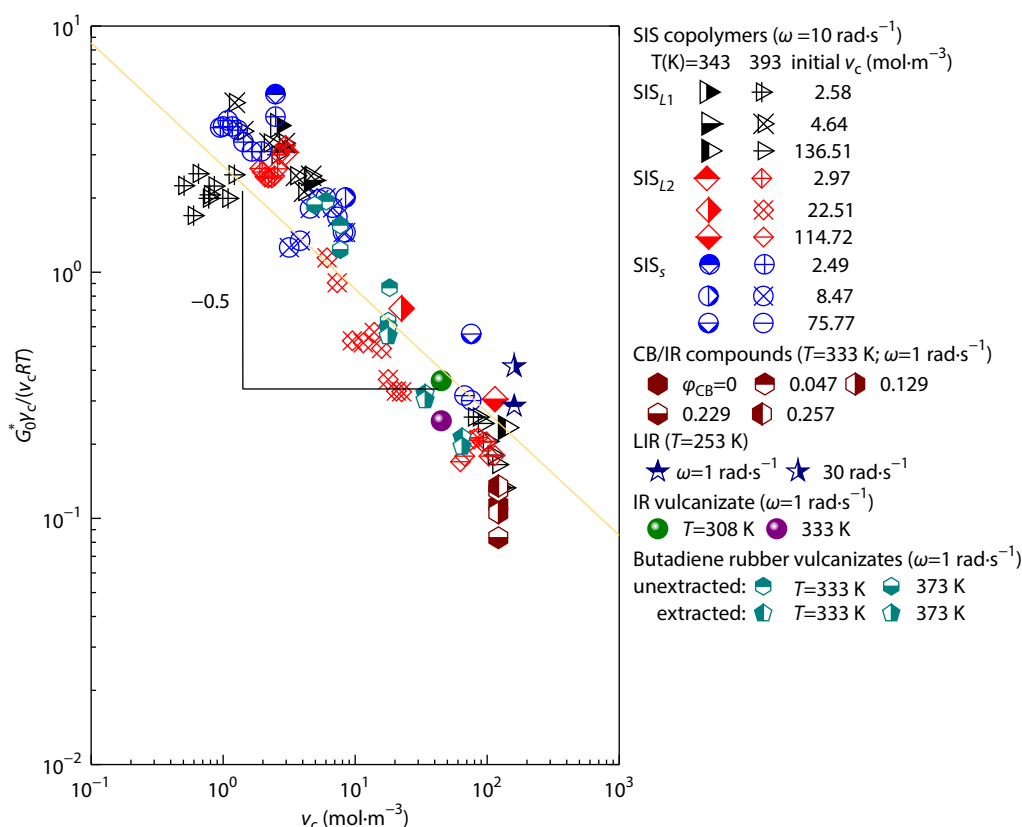


Fig. 8 $G^*_{0}v_c/(v_cRT)$ as a function v_c for SIS and several rubber gums, compounds and vulcanizates. For SIS at 343 K, v_c is determined by swelling in isooctane. For SIS tested at 393 K, the n^{th} -cycle v_c is estimated according to $v_{c,1}G^*_{0,n}/G^*_{0,1}$ where $v_{c,1}$ is the initial v_c value. For IR compounds and LIR, v_c is number density of elastically active entanglement network strands calculated from G_e . For IR vulcanizate, v_c is $45 \text{ mol}\cdot\text{m}^{-3}$ determined by swelling using tetrahydrofuran. For butadiene rubber vulcanizates being either extracted or not, the v_c , v_c and G^*_{0} values are got from the published work.^[93] The line with a slope of -0.5 outlines the relationship between $G^*_{0}v_c/(v_cRT)$ and v_c .

CONCLUSIONS

Microphase separated SIS copolymers, whether if the PI phase is selectively crosslinked or not, demonstrate Payne effect sharing the mechanism common to rubber vulcanizates and compounds. The LAOS behavior of SIS below $T_{g,PS}$ is reversible but it is irreversible above $T_{g,PS}$. The onset of strain softening in SIS, gum vulcanizates and filled rubber compounds under LAOS can be triggered at the time scale of intrinsic Rouse relaxation of EANS. Considering the conformation change of EANS, a simple scaling law is proposed for critical softening stress as a function of effective crosslinking density, which is validated in a series of polymeric materials differing in structure.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

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