Influence of Liquid Isoprene Rubber on Strain Softening of Carbon Black Filled Isoprene Rubber Nanocomposites

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Abstract The reinforcement of rubbers by nanoparticles is always accompanied with enhanced dissipation of mechanical energy upon large deformations. Methods for solving the contradiction between improving reinforcement and reducing energy dissipation for rubber nanocomposites have not been well developed. Herein carbon black (CB) filled isoprene rubber (IR)/liquid isoprene rubber (LR) blend nanocomposites with similar crosslink density (\(\nu_c\)) are prepared and influence of LR on the strain softening behaviors including Payne effect under large amplitude shear deformation and Mullins effect under cyclic uniaxial deformation is investigated. The introduction of LR could improve the frequency sensitivity of loss modulus and reduce critical strain amplitude for Payne effect and loss modulus at the low amplitudes. Meanwhile, tuning \(\nu_c\) and LR content allows reducing mechanical hysteresis in Mullins effect without significant impact on the mechanical performances. The investigation is illuminating for manufacturing nanocomposite vulcanizates with balanced mechanical hysteresis and reinforcement effect.

Keywords Rubber nanocomposites; Stress softening; Mechanical hysteresis; Liquid rubber

EXPERIMENTAL

Materials

Liquid isoprene rubber (LR, trademark LIR-30) with weight-averaged molecular weight of 30 kg/mol, polydispersity of 1.10, and glass transition temperature (\(T_g\)) of \(-65.3^\circ\text{C}\) (Fig. S1a in the electronic supplementary information, ESI) was purchased from Kuraray Co., Ltd., Japan. Isoprene rubber (IR, trademark IR2200) with more than 98% cis-1,4 structure, weight-averaged molecular weight of 1220 kg/mol and polydispersity of 2.0 was produced by Zeon Chem., Japan. Carbon black (N330) with particle size about 30 nm was purchased from Longxin Chem. Stock Co., Ltd., China. Sulfur and antioxidant of \(N\)-(1,3-...
dimethylbutyl)-N-phenyl-p-phenylenediamine (6PPD) were obtained from Kunshan Anzhe Chem. Stock Co., Ltd., China and Zhejiang Yongji Chem. Plant, China, respectively. Activator zinc oxide (ZnO) and stearic acid were purchased from Shanghai Macklin Biochem. Co., Ltd., China and Tokyo Chem. Co., Ltd., Japan, respectively. Accelerator N-cyclohexyl-2-benzothiazole-sulfenamide (CZ) was purchased from Aladdin, China.

**Sample Preparation**

Table 1 lists formulations of the nanocomposites. The IR gum was first mixed with 1 phr (parts per hundred parts of rubber) 6PPD, 2.5 phr steric acid and 4 phr ZnO (not included in Table 1) at 100 °C and 40 r/min for 10 min via an internal mixer (XSS-300, Kechuang Rubber Plastic Mechan. Equipment Co., Ltd., China). After adding LR and CB, the compounds were mixed at 100 °C and 40 r/min for 20 min. Finally, CZ and sulfur were added in the compounds at 80 °C and 30 r/min for 10 min.

| Table 1 Formulations of the compounds and their curing time for preparation of the vulcanizates. |
|-----------------------------------------------|
| Sample | IR | LIR-30 | CB | CZ | S | Curing time (min) |
| IR/OLR-20CB | 100 | – | 20 | 0.55 | 0.55 | 45 |
| IR/OLR-40CB | 100 | – | 40 | 0.55 | 0.55 | 43 |
| IR/OLR-60CB | 100 | – | 60 | 0.55 | 0.55 | 50 |
| IR/0.4LR-20CB | 71.4 | 28.6 | 20 | 0.95 | 0.95 | 43 |
| IR/0.4LR-40CB | 71.4 | 28.6 | 40 | 1.00 | 1.00 | 45 |
| IR/0.4LR-60CB | 71.4 | 28.6 | 60 | 1.05 | 1.05 | 37 |

* Amounts of raw materials and chemicals are presented in phr.

The carbon black gel (CBG) in the highly filled compounds was obtained via extraction experiment. The uncured compounds were extracted by toluene for 10 days and by renewing toluene every 2 days. At low CB contents, intact CBG could not be obtained due to the leakage of CB particles into solvent and the dissolution of the rubber.

To prepare nanocomposite vulcanizates, the compounds were compressed into sheets of 2 mm in thickness at 140 °C by a vulcanizer (XL-25, Huzhou Xinli Rubber Machinery Co., Ltd., China). The curing time (Table 1) was prescribed as the optimal vulcanization time determined from dynamic vulcanization curves.

The compounds, CBG and vulcanizates were named as IR/LR/CB-C, IR/IR/CB-CBG and IR/IR/CB-V, respectively. Here the letters “i” and “j” represent the ratio of LR to IR and the content of CB in phr, respectively, and “z” stands for cross-linking density (νz) of the matrix in mol/m³. For better comparison, νz was manipulated to be similar for vulcanizates with the same CB contents. For manipulating the mechanical hysteresis in cyclic deformations, vulcanizates with higher νz or LR to IR ratio were also prepared (Table S1 in ESI) by curing for 23, 21 and 32 min, respectively.

**Characterizations**

The dispersion of CB in the matrix was observed by transmission electron microscope (TEM, JEM-1200EX, JEOL, Japan) at an accelerating voltage of 300 kV. The samples were obtained by ultramicrotomy.

Toluene was used to swell the vulcanizates at room temperature for 48 h. Flory-Rehner equation \( \nu_s = \frac{\ln(1 - \nu_s) + \nu_s + \chi V_s^2/2(V_0(V_s^{1/2} - V_s^{1/2}))}{1} \) was utilized to calculate νs. Here \( V_s, V_0, \) and \( \chi \) are the molar volume of solvent (105.7 ml/mol), volume fraction of rubber in swollen samples and polymer-solvent interaction parameter estimated by 0.427+0.112V_s, respectively.[60]

The weight percentage of bound rubber in the compound and CBG was determined by weighing method. Thermogravimetric analysis (TGA, Q1000, TA Instruments, USA) was also applied to estimate the bound rubber content in CBG. Samples were heated from room temperature to 800 °C at a rate of 10 °C/min in nitrogen atmosphere.

Modulated differential scanning calorimetry (MDSC, Discovery 25, TA Instruments, USA) was used to test increment of heat capacity (ΔCp) of the nanocomposites across glass transition of the matrix. The samples after equilibration at ~85 °C for 5 min were heated to ~45 °C at a rate of 1 °C/min with modulated signal time of 2 min and amplitude of ±1 °C. The bound layer content was calculated according to 1-ΔCp/[1-(1-w)ΔCp(IR)]. Here w is the CB weight fraction in the nanocomposites and ΔCp(IR) is the increment of heat capacity of the matrix during glass transition.

Molecular weight and polydispersity of the sol fractions extracted from the compounds were measured by a gel permeation chromatography (GPC, Water 2690, Water Co., USA) at 40 °C and flow rate of 1 mm/min. Tetrahydrofuran was used as solvent.

The rheological behaviors of the compounds and vulcanizates were measured by a rheometer (ARES-G2, TA Instruments, USA) at 60 °C. The linear rheological responses were measured in the frequency (ω) range from 100 rad/s to 0.025 rad/s at strain amplitude (γ) of 0.1%. The strain amplitude sweep experiment was conducted in the ω range from 0.01% to 80% at 1 rad/s.

Dumbbell shaped samples of 4 mm in width, 2 mm in thickness and 25 mm in length of working section were used for tensile test using a tester (Sun’s Zongheng Technol. Co., Ltd., Shenzhen, China) at room temperature and at a crosshead velocity of 500 mm/min. The cyclic loading-unloading uni-axial tensile deformations with increasing maximum prestrains at each cycle were performed at step strain of 100% at crosshead velocity of 50 mm/min. The area of hysteresis loop in one loading-unloading cycle and that under the loading stress curve are defined as Ei and E respectively, and Ei/E is used to describe the ratio of energy dissipation in each cycle.

**RESULTS AND DISCUSSION**

**Microstructure and Interfacial Interaction of the Nanocomposites**

Fig. 1 shows TEM images of the vulcanizates. The CB nanoparticles are distributed rather homogeneously in the matrix. The degree of CB agglomeration increases at high CB contents while the composition of the matrix does not influence the CB dispersity significantly. The presence of LR has no influence on the distribution of other additives such as ZnO activator (Fig. S2 in ESI).

The adsorption of chains on the surface of CB nanocomposites leads to the formation of bound rubber depending on chains size[41-42] and filler content.[43,44] The bound rubber and CB constitute CBG in which a small fraction of strongly immobilized chains forms a thin glassy layer surrounding CB.

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nanoparticle. As shown in Table 2, \( T_g \) of bound rubber in the CBG is the same as that of the matrix (Fig. S1 in ESI). The CBG contains about 30% bound rubber (Table 2 and Fig. S3 in ESI), being independent of filler content and rubber composition. Normalized increment of heat capacity, \( \Delta C_p/(1-w) \), is about 0.36 J/(g·°C), which corresponds to glassy layer content less than 10% (Table 2), indicating a slight degree of chain immobilization.

The sol fraction extracted from the IR/0LR-20CB-C, IR/0.4LR-40CB-C and IR/0.4LR-60CB-C compounds demonstrates bimodal distribution (Fig. S4 in ESI), from which the content of the low molecular weight fraction is determined as 46.3%, 32.6% and 38.5%, respectively, being higher than that of LR in the matrix (28.6%) of the compounds. It indicates that long chains participate in the bound rubber formation preferentially.

The introduction of LR leads to the formation of more chain ends and more sulfur is required to maintain \( \nu_c \), the same as that of the IR vulcanizates at given CB contents (Table 1 and Table 3). The presence of LR raises the sol content slightly (Table 3) while most of chains are connected to the crosslinking network. Although \( \nu_c \) and CB contents are different, \( T_g \) and \( \Delta C_p/(1-w) \) of the vulcanizates are similar (Table 3; DSC curve referencing to Fig. S1 in ESI). Thus, the influences of \( T_g \) and glassy chains on the rheological and deformation behaviors will not be considered further.

**Rheological Behaviors of the Nanocomposites**

The introduction of CB significantly influences the linear rheological behavior of the uncured compounds (Fig. 2). For the compounds with IR or IR/0.4LR matrix, the frequency (\( \omega \))-dependencies of storage modulus (\( G' \)) and loss modulus (\( G'' \)) weaken gradually with increasing CB content. The presence of LR lowers both \( G' \) and \( G'' \). The variations of linear rheological behavior could be ascribed to the strain amplification effect induced by CB and the bound rubber formation at high CB contents. LR could reduce the bound rubber content slightly. In the IR/0LR-40CB-C, IR/0.4LR-40CB-C, IR/0LR-60CB-C and IR/0.4LR-60CB-C compounds, the bound rubber contents are 18.3%, 16.7%, 29.5% and 26.2%, respectively. However, both the segmental dynamics (Table 2) and bound rubber content are not determinative influencing factors of the rheological behaviors.

Fig. 3 shows nonlinear Payne effect of IR/0LR-JCB-C and IR/0.4LR-JCB-C compounds. Both \( G' \) and \( G'' \) are invariant in the low \( \gamma \) region (the values being denoted as \( G_0' \) and \( G_0'' \), respectively) while they decay markedly at \( \gamma \) above a critical amplitude (\( \gamma_c \)). The additions of CB and LR lower \( \gamma_c \). Fig. 4

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**Table 2** \( T_g \) and composition of CBG.

| CBG                  | \( T_g \) (°C) | \( \Delta C_p/(1-w) \) [J/(g·°C)] | Glassy layer content (%) | Rubber content (wt%) | Weighting | TGA |
|----------------------|--------------|----------------------------------|--------------------------|----------------------|-----------|-----|
| IR/0LR-40CB-CBG      | -67.4        | 0.362                            | 2.1                      | 31.3                 |           |     |
| IR/0.4LR-40CB-CBG    | -67.4        | 0.364                            | 7.8                      | 29.5                 |           |     |
| IR/0LR-60CB-CBG      | -67.2        | 0.371                            | ND \*                    | 33.0                 |           |     |
| IR/0.4LR-60CB-CBG    | -67.3        | 0.362                            | 8.3                      | 30.4                 |           |     |

\* Not detectable.

**Table 3** Parameters of the vulcanizates.

| Sample               | \( \nu_c \) (mol/m\(^3\)) | Sol content (wt%) | \( T_g \) (°C) | \( \Delta C_p/(1-w) \) [J/(g·°C)] |
|----------------------|----------------------------|-------------------|--------------|----------------------------------|
| IR/0LR-20CB-V\(_{64.3}\) | 64.3±1.4                  |                  |              |                                  |
| IR/0LR-40CB-V\(_{76.5}\) | 76.5±1.6                  |                  |              |                                  |
| IR/0LR-60CB-V\(_{110.4}\) | 110.4±4.7                 |                  |              |                                  |
| IR/0.4LR-20CB-V\(_{70.1}\) | 70.1±3.3                  |                  |              |                                  |
| IR/0.4LR-40CB-V\(_{79.3}\) | 79.3±4.1                  |                  |              |                                  |
| IR/0.4LR-60CB-V\(_{111.8}\) | 111.8±0.1                 |                  |              |                                  |

Fig. 1 TEM images of IR/0LR-20CB-V\(_{64.3}\) (a), IR/0LR-40CB-V\(_{76.5}\) (b), IR/0LR-60CB-V\(_{110.4}\) (c), IR/0.4LR-20CB-V\(_{70.1}\) (d), IR/0.4LR-40CB-V\(_{79.3}\) (e), and IR/0.4LR-60CB-V\(_{111.8}\) (f). The red circles indicate ZnO particles.
shows the normalized plots of $G'/G'_0$ and $G''/G''_0$ as a function of $A_γ$. Here $A_γ$ is strain amplification factor that is determined as horizontal shifting factor for creating master curves with reference to the nonlinear rheological curves of the matrix. It can be observed that $A_γ$ increases with filler content and is smaller in the IR/0.4LR compounds than in the IR/0LR ones (inset in Fig. 4). It means that the occurrence of Payne effect may be influenced by the molecular weight distribution of the matrix. It should be noted that, at 40–60 phr CB, the compounds demonstrate a two-step softening and the first
one occurred at $\gamma=1\%−10\%$ is more obvious for the IR/0.4LR compounds. The first softening is possibly related to breakup of some filler structures.\[47\]

LR influences the linear and nonlinear rheological responses of the nanocomposites vulcanizates. Fig. 5 illustrates $G'$ and $G''$ as a function of $\omega$. The $\omega$-sensitivities of $G'$ and $G''$ are much weaker than those of the compounds. The presence of LR lowers $G'$ on the one hand and improves the $\omega$-sensitivity of $G''$ on the other hand. Fig. 6 shows Payne effect of the vulcanizates. The $G''$ curves demonstrate weak strain overshoot (type III behavior), which differs from the sustain softening (type I behavior) of the compounds (Fig. 3). With increasing filler content, $\gamma_c$ becomes smaller and the weak strain overshoot becomes weaker.

Fig. 7 shows normalized plots of $G'/G_0'$ and $G''/G_0''$ as a function of $A_\gamma$. The superposition is well for $G'/G_0'$ while fails for $G''/G_0''$, exhibiting weak strain overshoot. The normalized plots of $G'/G_0'$ of the vulcanizates even overlap that of the uncured gum, suggesting that the crosslinking and filling do not alter the major mechanisms of the $G'$ decay accompanying the Payne effect. However, $A_\gamma$ in IR/0.4LR-CB vulcanizates is higher than that in the IR/0LR-CB vulcanizates at given CB contents, which is in contradiction with the compounds (Fig. 4). In the nonlinear region, $G'$ varies as $\gamma^x$ with $x=1.1$ and $x=1.3$ for the IR/0LR-CB and IR/0.4LR-CB vulcanizates, respectively. The scaling exponents are close to those in the uncured compounds (Fig. 4) and in silica filled polydimethylsiloxane vulcanizates,\[48\] being in agreement with the predictions ($x=4/3$\[49\] and $x=1$\[50\]) of Rouse model, revealing the importance of Rouse dynamics to the occurrence of Payne effect.

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**Fig. 5** $G'$ and $G''$ as function of $\omega$ for vulcanizates.

**Fig. 6** $G'$ (solid symbols, a and b), $G''$ (hollow symbols, a and b) and $\tan\delta$ (half-filled symbols, c and d) as a function of $\gamma$ for IR/0LR-CB-V$_\gamma$ (a and c) and cured IR/0.4LR-CB-V$_\gamma$ vulcanizates (b and d).
Uniaxial Tensile Deformation of Vulcanizates

Fig. 8 shows stress-strain curves of vulcanizates. At given CB contents and similar $v_e$, the presence of LR does not impair the mechanical performances. The vulcanizates during cyclic deformation demonstrate Mullins effect characterized by mechanical hysteresis and stress softening (Fig. 9). At given strains, the unloading stresses of the IR/0.4LR-CB-V$_{20}$ vulcanizates are higher than those of the IR/0.4LR-CB-V$_{40}$ ones. The differences become smaller with increasing CB content. Both $E_e$ and $E_h$ increase with increasing CB content and prestrain whereas the existence of LR reduces $E_e$ and relative hysteresis energy $E_h/E$ (Fig. 10). In filled vulcanizates, the physical interactions would be interrupted during loading and reform partially during the unloading process, which contributes to the Mullins effect. The introduction of LR in the nanocomposites has no influence on the filler-rubber interactions as evidenced by the small amount of glassy content and the similar bound rubber content (Table 2). Furthermore, LR has no influence on the filler dispersion (Fig. 1). It means that the reductions in $E_e$ and $E_h$ are not determined by the variations in filler structure and interfacial interaction. Such result highlights the vital role of rubber network structures including entanglement density, defect chains and $v_e$ on the stress softening, which is in contradiction with previous arguments that the mechanical hysteresis mainly involves in the destruction of filler structure and interfacial interactions.[1631–98] In the nanocomposites, LR participates in the crosslinking network formation, which is expected to generate a great number of dangling chains along with the production of a slightly increased sol fraction (Table 3). The LR chains connecting the CB nanoparticle and the rubber network should recoil prior to the long IR chains during the unloading process, promoting the hysteretic recovery of the deformation and lowering $E_h/E$.

Since the mechanical hysteresis is mainly related to rubber network, it could be tuned via regulating the LR content and $v_e$ at given CB loadings (Table S1 in ESI). At similar $v_e$, for the 60 phr CB filled vulcanizates, the introduction of LR has little effect on tensile strength and strain at break (Fig. S5 in ESI). At $v_e$=200 mol/m$^3$ and 60 phr CB, LR does not influence the loading stress while improves the unloading stress, promotes the hysteretic recovery and largely reduces $E_h/E$ at high prestrains (Figs. S6 and S7 in ESI). At $v_e$=116 mol/m$^3$ and 60 phr CB, $E_h/E$ at high prestrains decreases markedly with the increasing LR to IR ratio (Fig. 10c and Fig. S7c in ESI). Thus, the use of LR in combination with filling and crosslinking provides a potential way to prepare rubber nanocomposites with balanced mechanical performance and energy dissipation.

It is shown that the introduction of LR brings a promising balance between the mechanical hysteresis and reinforcement for the IR nanocomposite vulcanizates. The introduction of LR would bring complicated variations in molecular structure of the crosslinking network. It introduces structural heterogeneities associated with generation of chain branches and dangling ends that would restrain the molecular alignment along the stretch axis. The local crosslinking density and network defects in the vulcanized matrix should possibly contribute to the reduced energy dissipation in cyclic deformation. It is expected that the effects of LR should be dependent on the weight ratio of LR to IR, the molecular weight and its distribution of LR, and the competitive interactions of CB, sulfur and the other additives with LR and IR, which should be
investigated in detail in future.

CONCLUSIONS

It is a challenge to prepare rubber nanocomposites with high reinforcement efficiency and low energy dissipation. This long-standing issue is settled herein by using LR in CB filled IR vulcanizates. LR does not influence the filler-rubber interaction and the formations of glassy layer and bound rubber while it improves the $\omega$-dependence of $G''$ and the critical strain amplitude of Payne effect. By changing $v_c$ and/or LR content, the Mullins effect can be tuned, and the accompanied mechanical hysteresis can be reduced without significant influence on the mechanical performances.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://doi.org/10.1007/s10118-021-2550-y.
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REFERENCES
1 Guth, E. Theory of filler reinforcement. J. Appl. Phys. 1945, 16, 20–25.
2 Mooney, M. The viscosity of a concentrated suspension of spherical particles. J. Colloid Sci. 1951, 6, 162–170.
3 Krieger, I. M. Rheology of monodisperse latices. Adv. Colloid Interface Sci. 1972, 3, 111–136.
4 Schroyen, B.; Swan, J. W.; van Puyvelde, P.; Vermant, J. Quantifying the dispersion quality of partially aggregated colloidal dispersions by high frequency rheology. Soft Matter 2017, 13, 7897–7906.
5 Kraus, G. Mechanical losses in carbon-black-filled rubbers. Appl. Polym. Symp. 1984, 75–92.
6 Zhu, Z.; Thompson, T.; Wang, S. Q.; Von Meerwall, E. D.; Halasa, A. Investigating linear and nonlinear viscoelastic behavior using model silica-particle-filled polybutadiene. Macromolecules 2005, 38, 8816–8824.
7 Lewicki, J. P.; Maxwell, R. S.; Patel, M.; Herberg, J. L.; Swain, A. C.; Liggit, J. J.; Pethrick, R. A. Effect of meta-carboanil on segmental dynamics in a bimodal poly(dimethylsiloxane) network. Macromolecules 2008, 41, 9179–9186.
8 Song, Y.; Zheng, Q. Concepts and conflicts in nanoparticles reinforcement to polymers beyond hydrodynamics. Prog. Mater. Sci. 2016, 84, 1–58.
9 Payne, A. R.; Whittaker, R. E. Low strain dynamic properties of filled rubbers. Rubber Chem. Technol. 1971, 44, 440–478.
10 Payne, A. R.; Whittaker, R. E. Effect of vulcanization on low-strain dynamic properties of filled rubbers. J. Appl. Polym. Sci. 1972, 16, 1191–1212.
11 Diani, J.; Fayolle, B.; Gilromini, P. A review on the Mullins effect. Eur. Polym. J. 2009, 45, 601–612.
12 Nagaraja, S. M.; Mujtaba, A.; Beiner, M. Quantification of different contributions to dissipation in elastomer nanoparticle composites. Polymer 2017, 111, 48–52.
13 Robertson, C. G.; Wang, X. Isoenergetic jamming transition in particle-filled systems. Phys. Rev. Lett. 2005, 95, 075703.
14 Zhao, D.; Ge, S.; Senses, E.; Akcopra, P.; Jestin, J.; Kumar, S. K. Role of filler shape and connectivity on the viscoelastic behavior in polymer nanocomposites. Macromolecules 2015, 48, 5433–5438.
15 Cassagnau, P. Melt rheology of organoclay and fumed silica nanocomposites. Polymer 2008, 49, 2183.
16 Merabia, S.; Sotta, P.; Long, D. R. A microscopic model for the reinforcement and the nonlinear behavior of filled elastomers and thermoplastic elastomers (Payne and Mullins effects). Macromolecules 2008, 41, 8252–8266.
17 Majesté, J. C.; Vincent, F. A kinetic model for silica-filled rubber reinforcement. J. Rheol. 2015, 59, 405–427.
18 Steinert, S. S.; Zhu, A. J. Reinforcement mechanism of nanofilled polymer melts as elucidated by nonlinear viscoelastic behavior. Macromolecules 2002, 35, 7262–7273.
19 Li, Z.; Xu, H.; Xia, X.; Song, Y.; Zheng, Q. Energy dissipation accompanying Mullins effect of nitrile butadiene rubber/carbon black nanocomposites. Polymer 2019, 171, 106–114.
20 Hou, F.; Song, Y.; Zheng, Q. Payne effect of thermo-oxidatively aged isoprene rubber vulcanizates. Polymer 2020, 195, 122432.
21 Xu, H.; Xia, X.; Hussain, M.; Song, Y.; Zheng, Q. Linear and nonlinear rheological behaviors of silica filled nitrile butadiene rubber. Polymer 2018, 156, 222–227.
22 Li, Z.; Wen, F.; Hussain, M.; Song, Y.; Zheng, Q. Scaling laws of Mullins effect in nitrile butadiene rubber nanocomposites. Polymer 2020, 193, 123250.
23 Acosta, R. H.; Monti, G. A.; Villar, M. A.; Valles, E. M.; Vega, D. A. Transiently trapped entanglements in model polymer networks. Macromolecules 2009, 42, 4674–4680.
24 Agudelo, D. C.; Roth, L. E.; Vega, D. A.; Valles, E. M.; Villar, M. A. Dynamic response of transiently trapped entanglements in polymer networks. Polymer 2014, 55, 1061–1069.
25 Chasse, W.; Lang, M.; Sommer, J. U.; Saalwachter, K. Cross-link density estimation of PDMS networks with precise consideration of networks defects. Macromolecules 2012, 45, 899–912.
26 Campise, F.; Roth, L. E.; Acosta, R. H.; Villiar, M. A.; Valles, E. M.; Monti, G. A.; Vega, D. A. Contribution of linear guest and structural pendant chains to relaxational dynamics in model polymer networks probed by time-domain 1H NMR. Macromolecules 2016, 49, 387–394.
27 Bastra, A.; Cohen, C.; Archer, L. Stress relaxation of end-linked polydimethylsiloxane elastomers with long pendant chains. Macromolecules 2005, 38, 7174–7180.
28 Vega, D. A.; Villar, M. A.; Alessandrini, J. L.; Valles, E. M. Terminal relaxation of model poly(dimethylsiloxane) networks with pendant chains. Macromolecules 2001, 34, 4591–4596.
29 Yamazaki, H.; Takeda, M.; Kohno, Y.; Ando, H.; Urayama, K.; Takigawa, T. Dynamic viscoelasticity of poly(butyl acrylate) elastomers containing dangling chains with controlled lengths. Macromolecules 2011, 44, 8829–8834.
30 Urayama, K.; Miki, T.; Takigawa, T.; Kobijia, S. Damping elastomer based on model irregular networks of end-linked poly(dimethylsiloxane). Chem. Mater. 2004, 16, 173–178.
31 Li, Z.; Lu, X.; Tao, G.; Guo, J.; Jiang, H. Damping elastomer with broad temperature range based on irregular networks formed by end-linking of hydroxyl-terminated poly(dimethylsiloxane). Polym. Eng. Sci. 2016, 56, 97–102.
32 Yasuda, Y.; Minoda, S.; Ohashi, T.; Yokohama, H.; Ikeda, Y. Two-phase network formation in sulfur crosslinking reaction of isoprene rubber. Macromol. Chem. Phys. 2014, 215, 971–977.
33 Ikeda, Y.; Higashitani, N.; Hiiikata, K.; Kokubo, Y.; Morita, Y.; Shibayama, M.; Osaka, N.; Suzuki, T.; Endo, H.; Kobijia, S. Vulcanization: new focus on a traditional technology by small-angle neutron scattering. Macromolecules 2009, 42, 2741–2748.
34 Glebova, Y.; Reiter-Scherer, V.; Suvanto, S.; Korpela, T.; Pukkanen, T. T.; Severin, N.; Shershnve, V.; Rabe, J. P. Nano- mechanical imaging reveals heterogeneous cross-link distribution in sulfur-vulcanized butadiene-styrene rubber comprising ZnO particles. Polymer 2016, 107, 102–107.
35 Li, J.; Isaye, A. I.; Ren, X.; Soucek, M. D. Modified soybean oil extended SBR compounds and vulcanizates filled with carbon black. Polymer 2015, 60, 144–156.
36 Betron, C.; Cassagnau, P.; Bounor-Legare, V. Control of diffusion and exudation of vegetable oils in EPDM copolymers. Eur. Polym. J. 2016, 82, 102–113.
37 Li, Z.; Ren, W.; Chen, H.; Ye, L.; Zhang, Y. Effect of liquid isoprene rubber on dynamic mechanical properties of emulsion polymerized styrene/butadiene rubber vulcanizates. Polym. Int. 2012, 61, 531–538.
38 Ren, Y.; Zhao, S.; Li, Q.; Zhang, X.; Zhang, L. Influence of liquid isoprene on rheological behavior and mechanical properties of polysoprene rubber. J. Appl. Polym. Sci. 2015, 132, 41485.
39 Gruendken, M.; Velencoso, M. M.; Hirata, K.; Blume, A. Structure-propery relationship of low molecular weight 'liquid' polymers in blends of sulfur cured SBR-rich compounds. Polym. Test. 2020, 87, 106558.
40 Horkay, F.; Mckenna, G. B.; Deschamps, P.; Geissler, E. Neutron
scattering properties of randomly cross-linked polyisoprene gels. *Macromolecules* **2000**, *33*, 5215–5220.

41 Senses, E.; Akcora, P. Tuning mechanical properties of nanocomposites with bimodal polymer bound layers. *RSC Adv.* **2014**, *4*, 49628–49634.

42 Liu, J.; Wu, Y.; Shen, J.; Gao, Y.; Zhang, L.; Cao, D. Polymer-nanoparticle interfacial behavior revisited: a molecular dynamics study. *Phys. Chem. Chem. Phys.* **2011**, *13*, 13058–13069.

43 Karatrantos, A.; Clarke, N. A theoretical model for the prediction of diffusion in polymer/SWCNT nanocomposites. *Soft Matter* **2011**, *7*, 7334–7341.

44 Zheng, X.; Sauer, B. B.; Vanalsten, J. G.; Schwarz, S. A.; Rafailovich, M. H.; Sokolov, J.; Rubinstein, M. Reptation dynamics of a polymer melt near an attractive solid interface. *Phys. Rev. Lett.* **1995**, *74*, 407–410.

45 Baeza, G. P.; Dalmas, F.; Dutertre, F.; Majeste, J. C. Isostructural softening of vulcanized nanocomposites. *Soft Matter* **2020**, *16*, 3180–3186.

46 Trinh, G. H.; Desloir, M.; Dutertre, F.; Majeste, J. C.; Dalmas, F.; Baeza, G. P. Isostructural softening of the filler network in SBR/silica nanocomposites. *Soft Matter* **2019**, *15*, 3122–3132.

47 Zhang, Q.; Xu, H.; Song, Y.; Zheng, Q. Influence of hydroxyl-terminated polybutadiene liquid on rheology of fumed silica filled cis-polybutadiene rubber. *Polym. Chem.* **2019**, *180*, 121709.

48 Xu, H.; Ding, L.; Song, Y.; Wang, W. Rheology of end-linking polydimethyloxsiloxane networks filled with silica. *J. Rheol.* **2020**, *64*, 1425–1438.

49 Subbotin, A.; Semenov, A.; Hadziioannou, G.; ten Brinke, G. Nonlinear rheology of confined polymer melts under oscillatory flow. *Macromolecules* **1996**, *29*, 1296–1304.

50 Sarvestani, A. S. Nonlinear rheology of unentangled polymer melts reinforced with high concentration of rigid nanoparticles. *Nanoscale Res. Lett.* **2010**, *5*, 791–794.

51 Fu, W.; Wang, L.; Huang, J.; Liu, C.; Peng, W.; Xiao, H.; Li, S. Mechanical properties and Mullins effect in natural rubber reinforced by grafted carbon black. *Adv. Polym. Tech.* **2019**, *2019*, 4523696.

52 Sodhani, D.; Reese, S. Finite element-based micromechanical modeling of microstructure morphology in filler-reinforced elastomer. *Macromolecules* **2014**, *47*, 3161–3169.

53 Stockelhuber, K. W.; Sviatkov, A. S.; Pelevin, A. G.; Heinrich, G. Impact of filler surface modification on large scale mechanics of styrene butadiene/silica rubber composites. *Macromolecules* **2011**, *44*, 4366–4381.

54 Yatsuyanagi, F.; Suzuki, N.; Ito, M.; Kaidou, H. Effects of secondary structure of fillers on the mechanical properties of silica filled rubber systems. *Polymer* **2001**, *42*, 9523–9529.

55 Bhattacharyya, S.; Sinturel, C.; Bahloul, O.; Saboungi, M. L.; Thomas, S.; Salvetat, J. P. Improving reinforcement of natural rubber by networking of activated carbon nanotubes. *Carbon* **2008**, *46*, 1037–1045.

56 Meissner, B.; Matějka, L. A structure-based constitutive equation for filler-reinforced rubber-like networks and for the description of the Mullins effect. *Polymer* **2006**, *47*, 7997–8012.

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