

Super Strong and Tough Elastomers Enabled by Sacrificial Segregated Network

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Abstract The integration of high strength and toughness concurrently is a vital requirement for elastomers from the perspective of long-term durability and reliability. Unfortunately, these properties are generally conflicting in artificial materials. In the present work, we propose a facile strategy to simultaneously toughen and strengthen elastomers by constructing 3D segregated filler network via a simple latex mixing method. The as-fabricated elastomers are featured by a microscopic 3D interconnected segregated network of rigid graphene oxide (GO) nanosheets and a continuous soft matrix of sulfur vulcanized natural rubber (NR). We demonstrate that the interconnected segregated filler network ruptures preferentially upon deformation, and thus is more efficient in energy dissipation than the dispersed filler network. Therefore, the segregated filler network exhibits better reinforcing effects for the rubber matrix. Moreover, the excellent energy dissipating ability also contributes to the outstanding crack growth resistance through the release of concentrated stress at the crack tip. As a result, the strength, toughness and fatigue resistance of the nanocomposites are concurrently enhanced. The methodology in this work is facile and universally applicable, which may provide new insights into the design of elastomers with both extraordinary static and dynamic mechanical performance for practical applications.

Keywords Elastomers; Nanocomposites; Segregated network; Sacrificial bonds; Mechanical properties

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INTRODUCTION

Elastomers, as a type of soft materials with the ability to perform large and reversible deformation, are acknowledged to be strategically indispensable materials owing to their extensive applications in various fields, such as gloves, tires, seals, etc.^[1–4] However, the complicated and harsh working environments in practical applications highly require sufficient tensile strength, toughness and fatigue resistance of elastomers to ensure long-term durability and reliability. Nevertheless, achieving a combination of these properties in artificial elastomers is exceedingly difficult.

It has been revealed that a critical strategy to improve the mechanical properties of materials is to enhance their energy dissipation ability under external loading.^[5–7] To date, several methodologies have been explored to increase the energy dissipation of elastomers. The most notable one is introducing nature-inspired sacrificial bonds (e.g. hydrogen bonds,^[6,8,9] host-guest interactions^[10,11] and metal coordination complexes^[12,13]) into polymer networks. Through the preferential rupture of sacrificial bonds upon deformation,

significant stress redistribution and energy dissipating can be achieved, therefrom to tremendously enhance the mechanical performance of the elastomers. For example, inspired by the cuticles of marine mussel byssus, Filippidi and co-workers incorporate sacrificial and reversible iron-catechol cross-links into an epoxy network, realizing simultaneous enhancement in the tensile strength, toughness and stiffness of the fabricated elastomer, yet without sacrificing its extensibility.^[14] Besides, sacrificial bonds are highly designable, and different types of sacrificial bonds can be combined to achieve better toughening effects. Guo and co-workers integrate weaker sacrificial hydrogen bonds and stronger Zn-based units into a single elastomer network, resulting in an elastomer with a combination of high strength, stretchability, and excellent crack growth resistance, benefiting from the cooperative energy-dissipating effect of these two different types of sacrificial bonds.^[15] However, above-mentioned methods usually involve sophisticated synthesis and solvent-based processing, which is deviated from the current concept of developing green materials. Besides, most sacrificial bonds are reversible associations with lower bond energy than covalent bonds, thus suffer from insufficient mechanical strength and low dissociation temperature (typically lower than 100 °C), which inevitably restrict the practical applications of the materials.^[16] To address these issues, a burgeoning and effective strategy is combining sacrificial strategy with biomimetic hierarchical

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structures. For examples, Gong and co-authors prepared a class of mechanically robust, multifunctional hydrogels by constructing bio-inspired lamellar structures with periodically alternating hard layers of polymerized surfactants and soft gel layers of interpenetrating networks containing sacrificial hydrogen bonds.^[17] Walther and co-authors fabricated a type of transparent and self-healing polymers featuring super toughness and stiffness by assembling quadruple hydrogen-bonding motifs bonded dynamic polymers with high-aspect-ratio synthetic nanoclays, mimicking the hierarchical brick-and-mortar structure of nacre.^[18] Despite these advances, hierarchical structures are anisotropic owing to the direction dependence of mechanical performance. Although this issue can be remedied by constructing three-dimensional interconnected structure through embedding low melting-point alloy (LMA) within continuous soft hydrogel or elastomer matrices,^[19,20] these 3D structures are usually generated at macro scale, thus have little reinforcing and toughening effects on the matrices, not to mention that these methods usually rely on some special techniques, which is complicated and not universal. Progress in this field urgently requires to discover new strategy that is simple and practical to enhance the overall mechanical properties of elastomers.

Segregated network is a kind of microscopic 3D interconnected structure in which the rigid fillers are oriented along the boundary between the polymer matrix particles. The ability to undergo strain-induced structural evolution of 3D segregated structures enables the development of advanced flexible strain sensors containing conductive fillers like carbon black, CNTs and graphene.^[21–28] However, the potential energy dissipation ability of the segregated network and its toughening and strengthening effects on elastomers have rarely been explored. Herein, a segregated network of graphene oxide (GO) is constructed in natural rubber (NR) matrix through a facile latex mixing method. Instead of uniform dispersion, the latex mixing method distributes graphene oxide along specific paths at the interfaces of rubber particles resulting in a microstructure having well-ordered GO segregated network in the NR matrix. The rigid GO segregated network can bear load and serve as sacrificial network that preferentially ruptures to dissipate energy. As a result, the strength, modulus, and toughness of NR are simultaneously enhanced. Moreover, the incorporation of rigid and interconnected GO segregated network can effectively slow down the crack propagation by releasing the stress concentration around the crack tip, thus greatly enhances the crack resistance of the materials.

EXPERIMENTAL

Raw Materials

Industrial graphene oxide gel (purity $\geq 97\%$) was purchased from Zhongke nano-era, China. NR latex (60 wt% solid content) was obtained from the Chinese Academy of Tropical Sciences. Curing reagents including sulfur, zinc oxide (ZnO), *N*-cyclohexyl-2-benzothiazole-sulfenamide (CZ), stearic acid (SA), and antioxidant *N*-iso-propyl-*N'*-phenyl-*p*-phenylenediamine (4010NA) were provided by Sichuan Haida Rubber Group Co., Ltd.

Preparation of NR/GO Nanocomposites with Segregated Network

The nanocomposites with segregated network of graphene oxide (NR/SGO) were prepared by a facile latex assembly method. Graphene oxide gel was dispersed in deionized water by sonicating to get a homogeneous suspension for subsequent mixing process. NR latex was compounded as per the formulation given in Table 1. The NR latex was mixed with the curing ingredients along with continuous stirring by a homogenizer for 1 h, all curing ingredients were stably and homogeneously dispersed in water by ball-milling. Then, the GO aqueous suspension was mixed with the compounded NR latex under vigorous stirring at various GO concentrations ranging from 0.1 phr to 5 phr (parts per hundred parts of gum) in NR. Subsequently, the blends were coagulated by adding saturated salt water and filtered. The obtained solids were washed thoroughly with deionized water and then dried in a vacuum oven at 40 °C to constant weight. Sample sheets with segregated network were obtained by directly compression curing at 143 °C for 13 min. For comparison, the nanocomposites with dispersed GO (NR/DGO) were fabricated by destroying the segregated structure through two-roll mixing before hot-pressing.

Table 1 Formulation of latex compound.

Ingredients	Parts by weight	
	Wet weight	Dry weight
Centrifuged latex (60 wt% solid content)	167	100
Potassium hydroxide solution (10%)	2.5	0.25
Potassium laurate solution (20%)	1.3	0.13
Sulfur dispersion (50%)	3.0	1.5
Zinc oxide dispersion (40%)	0.5	0.2
<i>N</i> -cyclohexyl-2-benzothiazolesulfenamide (50%)	1.6	0.8
<i>N</i> -iso-propyl- <i>N'</i> -phenyl- <i>p</i> -phenylenediamine (50%)	2.0	1.0
Stearic acid	–	1.5

Characterizations

The dispersion state of GO nanosheets within the NR matrix was examined by using a transmission electron microscope (TEM, FEI TecnaiG2 F20 S-TWIN). Mechanical properties were measured on a universal testing machine (Instron 5966) at room temperature with a cross-head speed of 500 mm·min^{−1}. The loading-unloading cycles were performed by a universal testing machine (Instron 5966) with extension rate of 100 mm·min^{−1}. Fracture tests were conducted using the classical single edge notch test with an extension rate of 6 mm·min^{−1}. The fracture energy (G_c) was calculated by the Greensmith method: $G_c = 6WC/\lambda_c^{1/2}$, where C is the notch depth, λ_c is the fracture strain of notched sample, W is the fracture energy calculated by integration of the stress-strain curve of an un-notched specimen until λ_c . The fatigue tests were conducted on prismatic specimens (60 mm in gage length, 25 mm in width, 2 mm in thickness) with an initial edge-notch of around 5 mm in depth. The specimens were subjected to tension-tension fatigue testing in MTS810 with a displacement-controlled mode at room temperature and the crack length was measured by vernier caliper every 5000 cycles.

RESULTS AND DISCUSSION

Preparation of NR/SGO Nanocomposites with Segregated Network

In order to obtain a segregated network of GO nanosheets in NR matrix, the nanofiller needs to be well aligned along the boundaries of rubber particles. For this purpose, we employ a facile latex mixing method as shown in Fig. 1. NR latex is compounded as per the formulation given in Table 1 through mechanical agitation. All curing ingredients processed by ball-milling can be evenly and steadily dispersed in water for several days which far exceeds the sample preparation period. Subsequently, GO aqueous suspension is mixed with compounded NR latex by mechanical agitation and sonicated for a few minutes to get a homogeneous NR/GO blends with various GO concentrations ranging from 0 phr to 5 phr, respectively. The hybrid blends are then coagulated with the addition of saturated NaCl solution. During this process, the stability of emulsion is destroyed, and latex particles are assembled into micro sized aggregates, while GO are pushed into the interstitial spaces of the rubber particles, thus leading to a stable suspension of NR/GO microparticles. Thereafter, the blends are filtrated and thoroughly washed with deionized water followed by drying. Finally, an elastomer film with a GO segregated network is obtained by directly hot-press at 143 °C.

We fabricate a series of elastomers with such structure by systematically changing the GO weight fraction. The elastomers are denoted as NR/SGO_x, the number *x* is the corresponding loadings of GO with a unit of phr. To illustrate the toughening and strengthening effects of segregated network, we also fabricate a series of control samples with dispersed GO by destroying the segregated network *via* two-roll mixing before hot-press, denoted as NR/DGO_x.

Morphology and Microstructure of NR/GO Nanocomposites

Transmission electron microscopy (TEM) is employed to clearly manifest the microstructure of GO nanosheets in NR matrix. It is noticed that in NR/SGO nanocomposites, GO nanosheets align along specific path on the boundaries of rubber particles, forming a well-ordered segregated network (Fig. 2a). Latex stage mixing makes it extremely difficult for GO nanosheets to enter into latex particles because of the higher internal viscosity of the latex particles.^[29] The subsequent coagulation process precipitate NR particles to assemble into micro sized aggregates, propelling GO nanosheets into the interstitial spaces of the rubber particles. After drying and vulcanizing, the spherical structure of rubber particles is disintegrated and fused to form a continuous rubber matrix, while GO nanosheets are further extruded to form a segregated network.^[30–32] In sharp contrast, GO nanosheets are uniformly distributed in NR/DGO samples after two-roll mixing (Fig. 2b), in which the segregated networks of GO are destroyed under the powerful dynamic shear force, leading to a uniform distribution of GO in the rubber matrix.

Energy Dissipation of NR/GO Nanocomposites

The incorporation of rigid nanofillers into soft rubber matrices typically allows the microstructure to dissipate more energy, as the added fillers are capable of absorbing polymer chains and acting as physical crosslinks. These physical crosslinks have relatively low bond energy compared with covalent bonds, thus they can preferentially break upon deformation to dissipate energy before failure of the materials, serving as sacrificial bonds.^[33] The feature of the sacrificial network in these nanocomposites, hysteresis, is visualized by the systematic loading unloading experiments to a predefined tensile strain ($\epsilon = 3$) on unfilled NR, fresh samples with dispersed GO network (NR/DGO₄) and segregated GO networks (NR/SGO₄), respectively. As

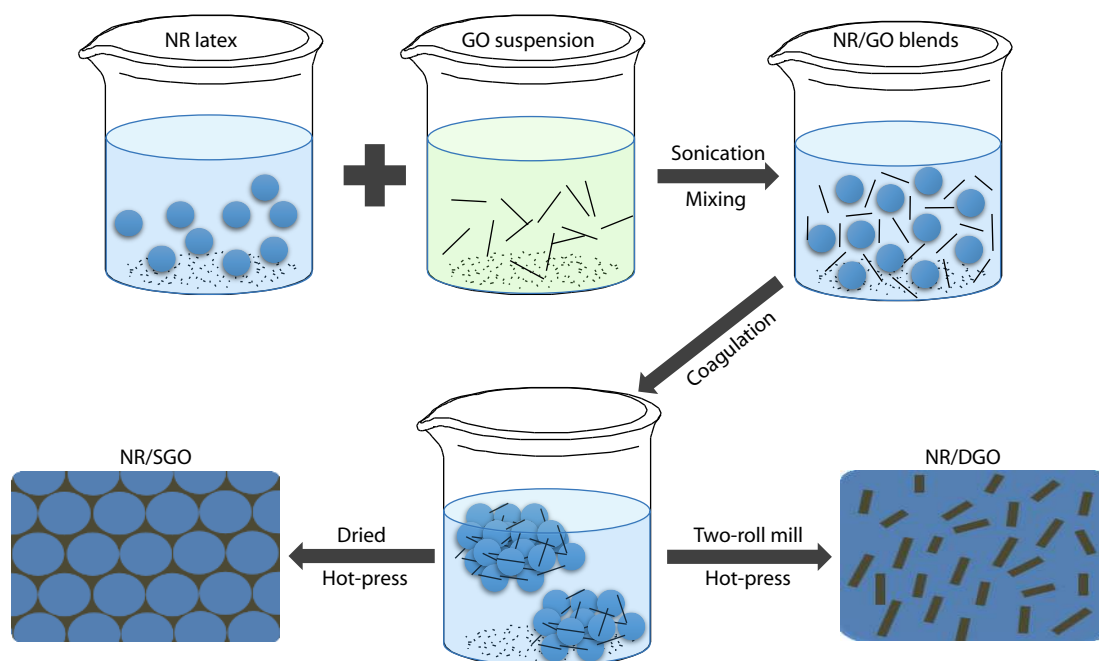


Fig. 1 Schematic representation for the preparation of NR/GO composites with segregated GO network (NR/SGO) and dispersed GO network (NR/DGO), respectively.

expected, unfilled NR is quite elastic with extremely low hysteresis in the first cycle (Fig. 3), which suggests only a small part of energy is dissipated during this process. This is reasonable for an unfilled polymer, of which the fracture energy arises from intrinsic dissipation (f_0) as polymer chains break.^[34,35] Significantly, the inclusion of fillers in polymer matrices can engineer additional energy dissipating modes through mechanisms including chain breakage at the interfaces between the rubber

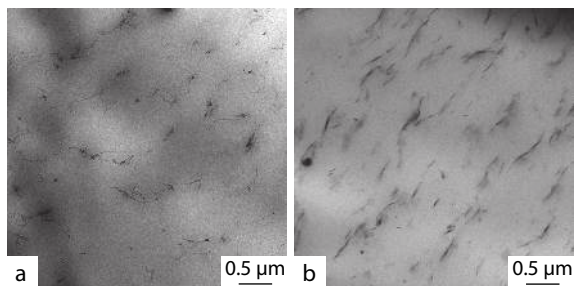


Fig. 2 TEM images of the NR/GO composites film showing (a) segregated network of GO in NR/SGO₄ and (b) dispersed network of GO in NR/DGO₄, respectively.

and the fillers, the detaching and slipping of polymer chains from the surfaces of fillers.^[36,37] Therefore, prominent hysteresis loops are observed in both NR/DGO and NR/SGO nanocomposites during the first cycle, indicating more energy is dissipated after the incorporation of rigid GO nanosheets. Nevertheless, further observation indicates that the microstructure of fillers in rubber matrix may also affect the energy dissipation process, as the hysteresis loop of NR/SGO₄ nanocomposite is much bigger than that of NR/DGO₄ nanocomposite, suggesting the segregated network can dissipate more energy under external loading than dispersed network.

Because the filler network undergoes substantial changes in the first cycle that cannot recovery in a short time, thus smaller hysteresis loop and energy dissipation efficiency can be found in the second cycle for all samples. However, the hysteresis loop of NR/SGO nanocomposites with segregated filler network is higher than that of NR/DGO nanocomposites with dispersed filler network in the second cycle. Interestingly, the hysteresis loop of NR/SGO nanocomposite in the second cycle is very similar to that in the first tensile cycle of NR/DGO nanocomposite (Fig. 4a). Moreover, the efficiency of energy dissipation, which is calculated as the ratio between

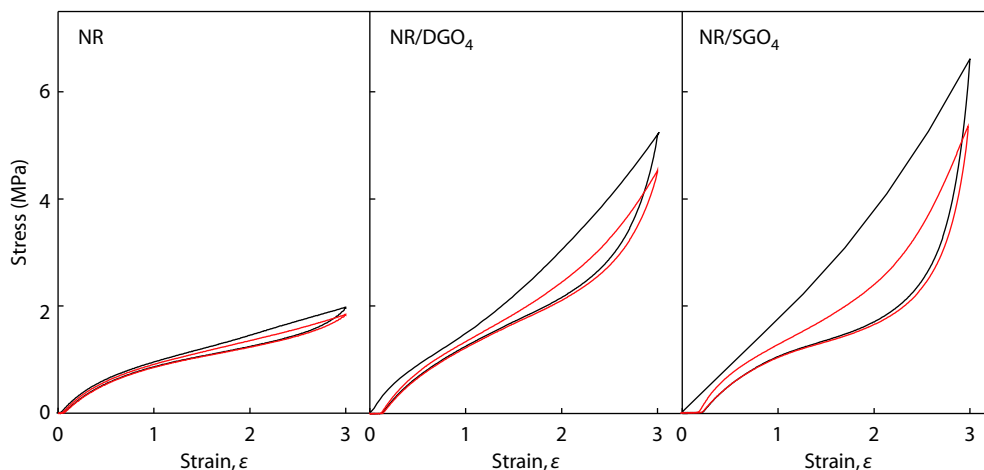


Fig. 3 Representative stress-strain curves of unfilled NR, NR/DGO₄ and NR/SGO₄ subjected to a cyclic uni-axial tension with a maximum strain of $\epsilon=3$. The black line corresponds to the first cycle; the red line corresponds to the second cycle.

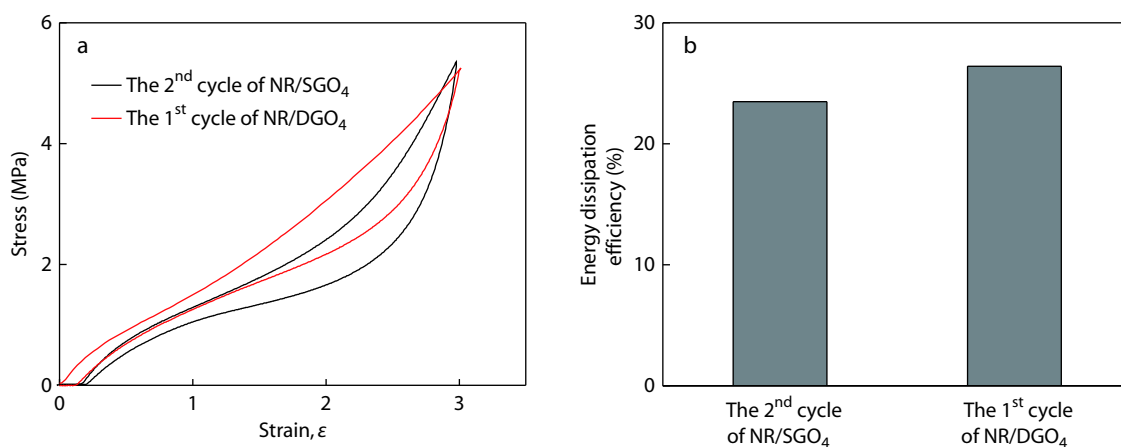


Fig. 4 The comparison of (a) the hysteresis loop and (b) energy dissipation efficiency between the 1st cycle of NR/DGO₄ and the 2nd cycle of NR/SGO₄ at a strain of 3.

the integrated area in the hysteresis loop and that under the loading curve, shows very small gap between the second cycle of NR/SGO and the first tensile cycle of NR/DGO (Fig. 4b). This phenomenon might be owing to the fact that the segregated structure of NR/SGO sample has already been destroyed during the first cycle and a dispersed network similar to that of original NR/DGO participates into the loading-unloading process of the second cycle.

The Mechanism of Energy Dissipation of NR/GO Nanocomposites

The underlying cause of such difference in energy dissipation is these two kinds of filler networks undergo different fracture processes upon deformation. For NR/DGO nanocomposites with dispersed GO network, aside from intrinsic dissipation, energy is mainly dissipated by slipping of adsorbed molecular chains from surfaces of fillers and detaching polymers from fillers upon deformation (Γ_D), thus the total energy dissipation is $\Gamma_T = \Gamma_0 + \Gamma_D$. For NR/SGO nanocomposites with segregated GO network, according to our previous study,^[38] the interconnected GO segregated network fractures preferentially upon deformation because of its smaller fracture strain compared with covalently crosslinked rubber networks, leading to massive energy dissipation (Γ_F). Moreover, the fracture of the segregated network is a progressive process rather than a catastrophic one, exhibiting repeated fractures at multiple regions from small to large strains. Accompanying this process, the morphology of filler network undergoes constant evolution from an interconnected segregated pattern to a dispersed distribution pattern, similar to the filler network in NR/DGO nanocomposites (Fig. 5a). As a result, the total energy dissipation for NR/SGO nanocomposites increases to $\Gamma_T = \Gamma_0 + \Gamma_D + \Gamma_F$ (Fig. 5b). Therefore, NR/SGO nanocomposites with sacrificial segregated network can dissipate much more energy than NR/DGO nanocomposites with dispersed GO network.

To better distinguish the energy dissipation capacity differences of the nanocomposites with segregated GO network from the nanocomposites with dispersed GO network, fresh samples were subjected to cyclic tensile tests to different

strains (Fig. 6). Clearly, the hysteresis loss of NR/SGO nanocomposites is much higher than that of NR/DGO nanocomposites when the GO loading is constant (Figs. 6a–6c). Moreover, the energy dissipation efficiency of NR/SGO nanocomposites is much higher than that of NR/DGO nanocomposites under every strain, especially under small strains where the strain induced crystallization (SIC) can be neglected (Figs. 6d–6f).

Interestingly, the energy dissipation efficiency of NR/DGO nanocomposites shows very subtle distinction at small strain ($\epsilon = 1$) with increasing filler loading, while sharp gap appears at higher strains (Fig. 7a). This phenomenon suggests that there is a strain threshold for the slipping of molecular chains from surface of fillers and detaching of polymers from fillers; only when this threshold is exceeded will drastic slipping and detaching occur. In sharp contrast, the energy dissipation efficiency of NR/SGO nanocomposites shows huge gaps at every strain with increasing filler loading (Fig. 7b), which is quite reasonable considering the strain threshold for the fracture of the interconnected segregated GO network is very small. Moreover, the efficiency of energy dissipation increases with the GO loading at a constant strain and increases with strain at a constant GO loading in all nanocomposites, as the higher GO loading provides more physical crosslinks and higher strain leads to the break of more physical crosslinks. In view of above-mentioned results, conclusion can be drawn that the segregated filler network is more efficient in energy dissipation than dispersed filler network. Given that hysteresis is highly important for a tough material, because it is a measure of toughness,^[39] we can conclude that constructing segregated network is an excellent approach to toughen elastomers.

Crack Growth of the NR/GO Nanocomposites

Rubber products are often subjected to dynamic loading conditions during their practical service, which puts forward high requirements for the crack resistance of rubber materials to ensure reliability and long-term durability. To investigate the crack growth resistance of NR/GO nanocomposites and the

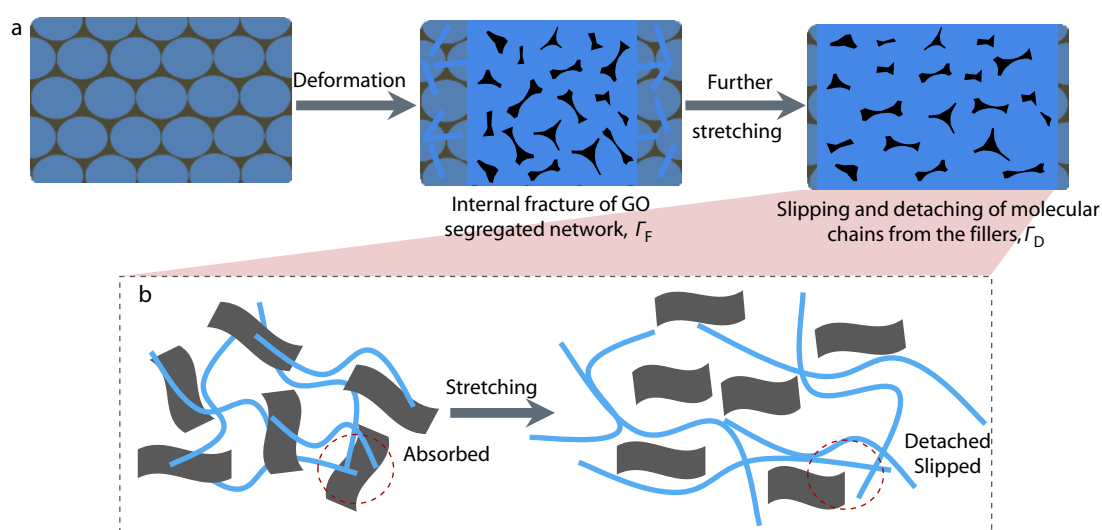


Fig. 5 Mechanisms of dissipating external mechanical work in NR/SGO samples. (a) The morphology evolution of GO segregated network during deformation. (b) Schematic illustration for the slipping and detaching of molecular chains from the fillers.

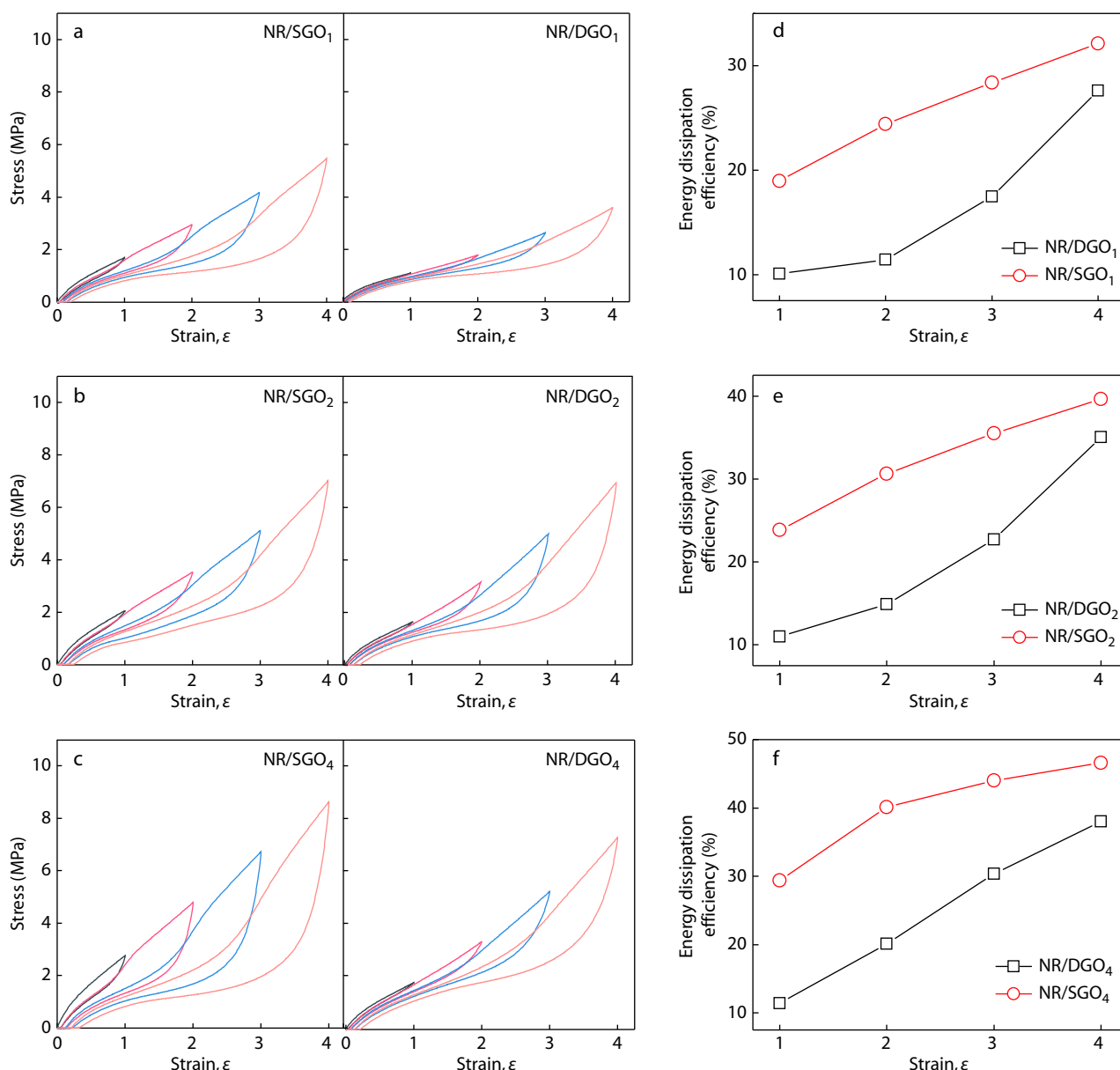


Fig. 6 Energy dissipation of NR/GO nanocomposites during the first tensile cycle. (a–c) Representative cyclic stress-strain curves of NR/SGO₁, NR/DGO₁, NR/SGO₂, NR/DGO₂, and NR/SGO₄, NR/DGO₄, respectively. (d–f) Energy dissipation efficiency of the first tensile cycle of NR/SGO₁, NR/DGO₁, NR/SGO₂, NR/DGO₂, and NR/SGO₄, NR/DGO₄, respectively.

influence of microstructure on the fatigue properties, a materials testing system (MTS810) is used to study the crack growth of unfilled NR, NR/DGO₂ nanocomposite and NR/SGO₂ nanocomposite under dynamic cyclic loading, and the plots of crack length versus fatigue cycles are presented in Fig. 8(a). Apparently, all NR/GO nanocomposites are better in resisting crack growth than the unfilled NR. For unfilled NR, the crack growth is fast from the very beginning of the fatigue test, and sharp increase in crack length occurs after 5.0×10^4 cycles. The incorporation of dispersed GO nanosheets slows down the crack growth rate to some extent, yet rapid crack growth still emerges after 7.5×10^4 cycles. Surprisingly, the crack growth in NR/SGO nanocomposites with segregated network is extremely slow even after 1.0×10^5 cyclic loadings, suggesting

extraordinary crack resistance. Quantitatively, the crack length growing rate is calculated and ranked at different levels (Fig. 8b), where level 1 to level 5 indicate the growing rate is 10% to 50% in relative to the initial crack length, respectively. When incorporating segregated GO network at a GO loading of 2 phr, the cycle number required to reach level 1 in NR/SGO₂ is approximately 2.5-fold compared to NR/DGO₂ nanocomposites with dispersed GO network and quadruples compared with those of the unfilled NR. In addition, the number of dynamic loading cycles required to reach the level 5 for NR/SGO₂ nanocomposite is much more than those of NR/DGO₂ nanocomposite and unfilled NR. This suggests that the NR/SGO nanocomposites can endure more cyclic loadings and have the longer lifetime than the unfilled NR and the nanocomposites

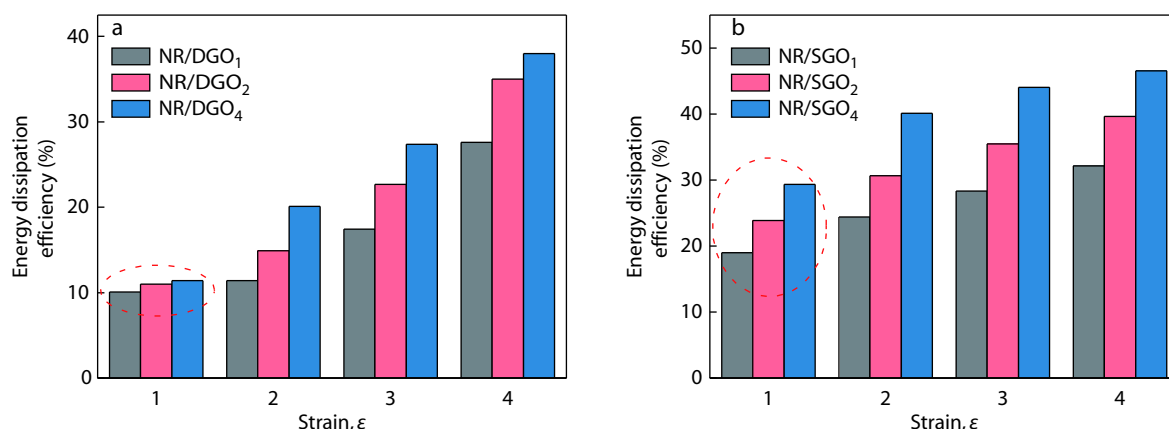


Fig. 7 (a) Energy dissipation efficiency of NR/DGO₁, NR/DGO₂, and NR/DGO₄ under different strains. (b) Energy dissipation efficiency of NR/SGO₁, NR/SGO₂, and NR/SGO₄ under different strains.

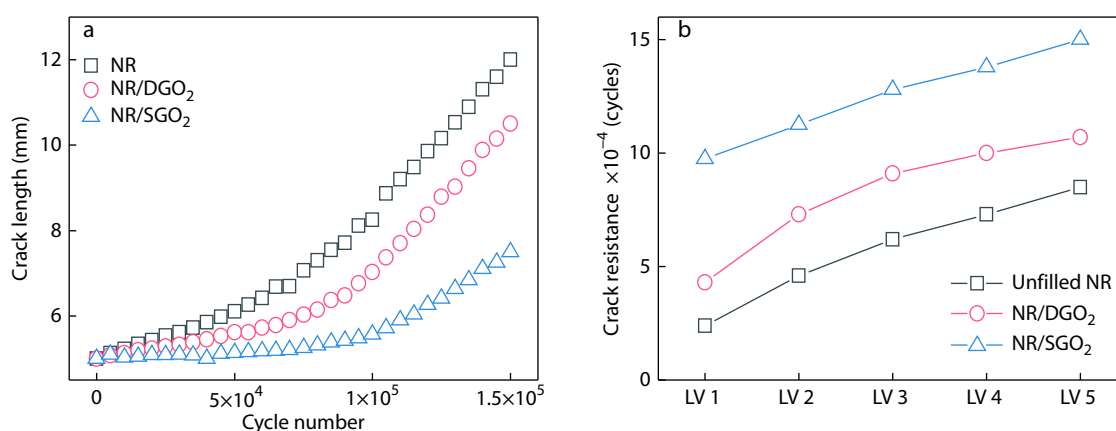


Fig. 8 Crack resistance of NR/GO nanocomposites with different microstructures. (a) Crack length versus the fatigue cycles for the unfilled NR and NR/GO nanocomposites. (b) Cracking resistance of unfilled NR, NR/DGO₂, and NR/SGO₂.

filled with dispersed GO nanosheets. Considering that all nanocomposites have exactly the same composition and undergo the same preparation process, the main reason for such significant difference in crack growth resistance ought to be the microstructures differences.

Accordingly, the ability to resist crack growth of elastomers is closely related to the energy dissipation during the propagation of pre-existing crack.^[40,41] Previous studies have precisely elucidated that the core mechanism and essential factor of crack propagation resistance in double network (DN) gels cause the large hysteresis ascribed to the internal fracture of the brittle network, which releases the stress concentration at the crack tip tremendously.^[42–44] In this case, the rigid filler network in NR/GO nanocomposites can serve as sacrificial network that preferentially ruptures to dissipate a lot of energy as demonstrated before, thus avoid the stress concentration at the crack tip and enhance crack propagation resistance. Therefore, the inclusion of rigid GO nanosheets dramatically improves the crack growth resistance of NR. As a matter of course, since it has already been proved that the segregated filler network far outperforms the dispersed filler network in energy dissipation, it is no wonder why NR/SGO nanocomposite is superior to unfilled NR and NR/DGO nanocomposite in crack resistance.

Mechanical Properties of NR/GO Nanocomposites

The formation of filler network is demonstrated experimentally to increase tensile strength, modulus, electrical conductivity and thermal stability, as well as decrease molecular mobility, flammability and gas permeability of elastomers.^[45–50] To explore the influence of microstructure on the mechanical performance of NR/GO nanocomposites, uniaxial tensile tests were carried out dumbbell shaped samples. The typical stress-strain curves of NR/SGO nanocomposites with segregated GO network and NR/DGO nanocomposites with dispersed GO network are shown in Figs. 9(a) and 9(b), respectively. The unfilled NR has a relatively low tensile strength of 16.5 MPa, which is severely insufficient for practical engineering applications. Significantly, the incorporation of rigid nanofillers pronouncedly increases the strength and modulus of all nanocomposites compared with unfilled NR no matter how these nanofillers distribute. Both tensile strength and modulus increase with increasing GO loading, and the optimum GO loading is 5 phr for maximizing the mechanical strength. Actually, the presence of GO nanosheets in the rubber matrix can offer resistance to the segmental movement of the polymer chains upon the application of the tensile stress, thus leads to the enhancement in modulus and strength.^[51] Nevertheless, further observation and comparison reveal that the microstructure of GO filler network also has a

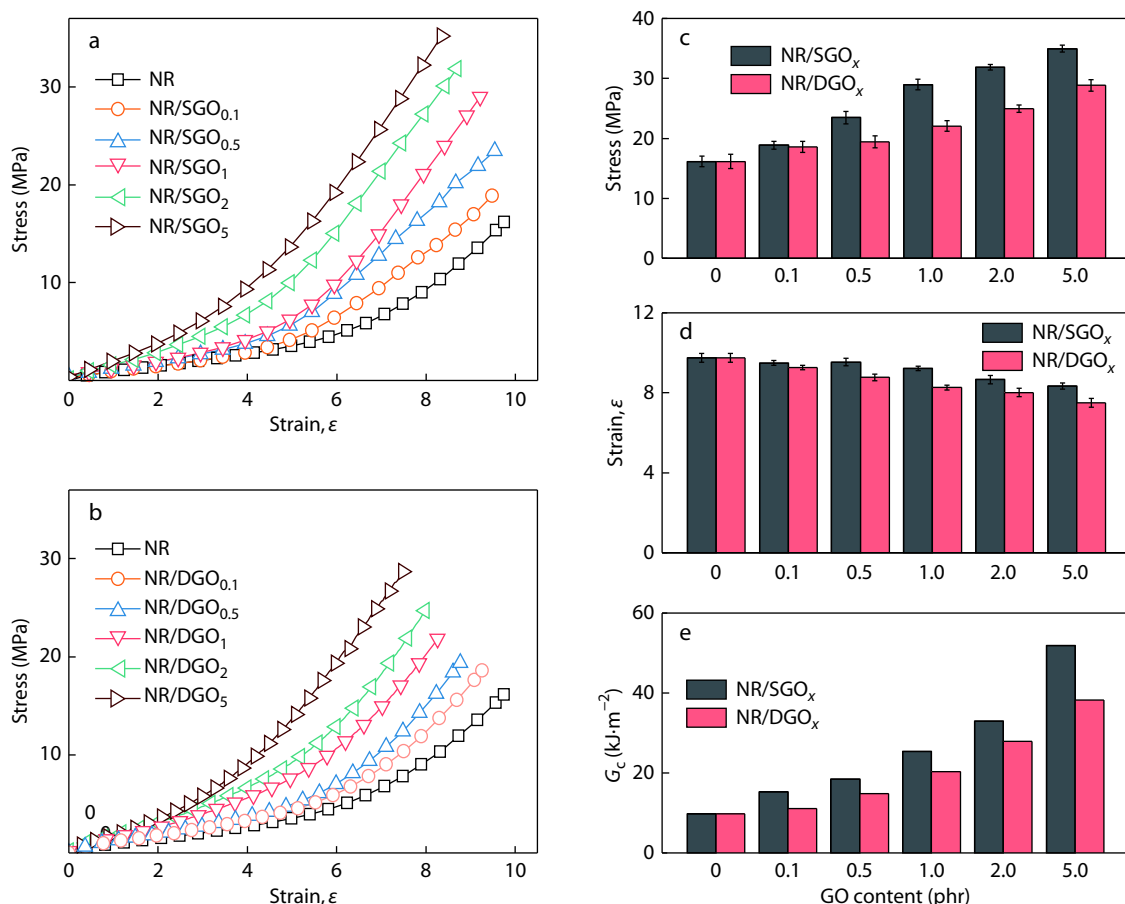


Fig. 9 Mechanical performance of NR/GS nanocomposites. (a) The stress-strain curves of NR/SGO nanocomposites with segregated GO network. (b) The stress-strain curves of NR/DGO nanocomposites with dispersed GO network. The comparison of (c) the ultimate strength, (d) fracture strain, (e) fracture toughness between NR/SGO nanocomposites and NR/DGO nanocomposites, respectively.

great influence on the mechanical properties of nanocomposites. NR/SGO nanocomposites with interconnected segregated network exhibit higher mechanical strength than NR/DGO nanocomposites with dispersed filler network, as shown in Fig. 9(c). Such differences in the mechanical properties can be explained in terms of the interconnected segregated GO network in the NR matrix, which can fracture upon deformation to help in dissipating a large amount of energy through the interface, thus bringing better ability to bear loading and resulting in better mechanical properties.

Generally, the increase in strength and modulus usually compromises the stretchability of the material. Therefore, the fracture strain shows a slight decrease with the increase of GO loading in all nanocomposites, and the microstructure has little influence on the fracture strain of the nanocomposites according to Fig. 9(d). Despite the decrease in fracture strain, the fracture toughness, which is calculated using the Greensmith method,^[52] shows astonishing improvement in both NR/DGO nanocomposites and NR/SGO nanocomposites as shown in Fig. 9(e). Unfilled NR has a fracture toughness of $9.82 \text{ kJ}\cdot\text{m}^{-2}$; after the incorporation of 5 phr GO nanosheets, the fracture toughness increases to $38.26 \text{ kJ}\cdot\text{m}^{-2}$ in NR/DGO₅ nanocomposites with dispersed filler network and

$51.89 \text{ kJ}\cdot\text{m}^{-2}$ in NR/SGO₅ nanocomposites with segregated network, which are improved by about 389% and 528% in comparison with unfilled NR, respectively. Obviously, the fracture toughness of NR/SGO nanocomposites with segregated network is higher than that of NR/DGO nanocomposites with dispersed filler network when extended for containing the same amount of GO nanosheets, which means that more energy is needed to break the segregated network compared to dispersed filler network.

By and large, the inclusion of rigid GO nanofillers network can significantly improve the strength, modulus and toughness of the elastomer simultaneously. However, obvious gap exists in mechanical properties between NR/SGO nanocomposites with segregated filler network and NR/DGO nanocomposites with dispersed filler network. In NR/SGO nanocomposites, the interconnected segregated network can fracture preferentially upon deformation to help in dissipating a large amount of energy, thus bringing better ability to bear loading. Meanwhile, the better crack growth resistance, along with the better energy dissipation performance of segregated network, all contribute to a much higher toughness of NR/SGO nanocomposites than that of NR/DGO nanocomposites.

CONCLUSIONS

In summary, we report a simple and effective approach to toughen and strengthen elastomers by constructing segregated network of GO. The facile latex mixing method is employed to obtain such segregated network. Latex stage mixing distributes GO sheets along specific pathway at the surface of latex particles, forming a well-ordered interconnected segregated network after film forming. The as-designed interconnected segregated network can serve as sacrificial network that ruptures prior to the permanent covalent rubber network under deformation, which effectively dissipates a lot of energy, thus bringing better ability to bear external load. Besides, the excellent energy dissipation performance of segregated network makes it extremely good at releasing the stress concentration at the crack tip, endowing the nanocomposite with great crack growth resistance. Consequently, the tensile strength, toughness and fatigue resistance of the resultant nanocomposites are simultaneously improved. The concept of designing interconnected segregated presented here is quite simple and scalable, and can be easily extended to other materials. This work provides a good basis for the preparation of elastomers with excellent mechanical properties under both static and dynamic conditions for practical uses that require long-term sustainability of materials.

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