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Cite this article as:

Liu Han, Huang Guang-Su, Wei Lai-Yun, Zeng Jian, Fu Xuan, Huang Cheng, Wu Jin-Rong. Inhomogeneous Natural Network Promoting Strain-induced Crystallization: A Mesoscale Model of Natural Rubber[J]. *Chinese J. Polym. Sci.*, 2019, 37(11): 1142-1151. doi: 10.1007/s10118-019-2267-3

View online: <https://doi.org/10.1007/s10118-019-2267-3>

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Inhomogeneous Natural Network Promoting Strain-induced Crystallization: A Mesoscale Model of Natural Rubber

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Abstract Although synthetic rubbers show continuously improved mechanical properties, natural rubber (NR) remains irreplaceable in the rubber family due to its superior mechanical properties. A mainstream viewpoint regarding the superiority of NR is that NR possesses a natural network formed by linking the poly(*cis*-1,4-isoprene) chain terminals to protein and phospholipid aggregates; after vulcanization, the natural network additionally contributes to rubber mechanics by both increasing the network density and promoting the strain-induced crystallization (SIC) behavior. However, the reason why the natural network promotes SIC is still unclear; in particular, only using the increased network density cannot explain our finding that the NR shows smaller onset strain of SIC than Gel (the gel component of NR with higher network density) and even vulcanized NR. Herein, we point out that the inhomogeneous chain deformation is the alternative reason why SIC of NR takes place at smaller strain than that of Gel. More specifically, although the natural network is homogenous on the subchain length scale based on the proton double-quantum NMR results, it is essentially inhomogeneous on mesoscale (100 nm), as revealed by the small angle X-ray scattering analysis. This inhomogeneous network also leads to the mesoscale deformation inhomogeneity, as detected by the orientation of stearic acid (SA) probe, thus resulting in the smaller onset strain of SIC of NR. Based on the experimental results, a mesoscale model is proposed to qualitatively describe the crucial roles of inhomogeneous structure and deformation of natural network in NR's mechanical properties, providing a clue from nature to guide the development of high-performance rubbers with controlled structures at mesoscale.

Keywords Natural Rubber; Inhomogeneous natural network; Strain-induced crystallization; Mesoscale model

Citation: Liu, H.; Huang, G. S.; Wei, L. Y.; Zeng, J.; Fu, X.; Huang, C.; Wu, J. R. Inhomogeneous natural network promoting strain-induced crystallization: A mesoscale model of natural rubber. *Chinese J. Polym. Sci.* 2019, 37, 1142–1151.

INTRODUCTION

Natural rubber (NR) possesses excellent mechanical properties, such as high tensile and tear strength, high crack growth resistance, good elasticity, and minimal heat build-up.^[1] These properties cannot be fully replicated in synthetic polyisoprene rubber (IR), even though IR has similar molecular weight and chain configuration to NR.^[2] In the last decades, much effort has been made to decipher the mystery why NR has superior mechanical properties to those of synthetic rubber.^[3–15] Now, it is widely accepted that natural network is the most critical factor that determines the superior mechanical properties of NR by both increasing network density and promoting strain-induced crystallization (SIC) behavior.^[12–15] As proposed by Tanaka and coworkers, the natural network is formed by linking the α and ω terminals of poly(*cis*-1,4-isoprene) chains to the phospholipid and protein aggregates, respectively.^[3–5,9,15] Based on this model at chain scale, a universal mechanism regarding the natural network promoting SIC has been revealed afterwards: the natural net-

work introduces numerous trapped entanglements into NR as network constraints, and the resulting increased network density leads to shorter subchains between local constraints that promote SIC.^[12] However, a present finding of NR reveals the limitation of this mechanism: NR exhibits smaller onset strain of SIC than some vulcanized NR does, which suggests network density is not necessarily the sole or main factor that promotes SIC.^[16]

Alternatively, structural inhomogeneity might be a possible reason leading to such an abnormal phenomenon. However, it has been revealed that the chain end-to-end distance between local constraints of NR shows unexpected homogeneous distribution.^[17] With such a confliction in mind, it is essential to explore the structural inhomogeneity on a larger scale, and to understand the structural features from microscale of 1–10 nm (typical end-to-end distance of subchains between local constraints)^[6,17–21] to mesoscale of 100 nm (typical diameter of chain cluster producing crystals at onset strain of SIC),^[11,19,22] thus to give more insights into the mechanism of why the natural network promotes SIC. Unfortunately, from the viewpoint of mesoscale, it is still unclear what inhomogeneity exists in the unvulcanized NR and whether/how the inhomogeneity affects its SIC. Nevertheless, in vulcanized rubber networks, much effort has been

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Received February 18, 2019; Accepted March 30, 2019; Published online June 6, 2019

made to explore their mesoscale structure and the relationships between the mesoscale structure and SIC/rubber mechanics.^[18–28] It is unraveled that the sulfur-vulcanized network is much more inhomogeneous than the peroxide-vulcanized network on mesoscale,^[18,23–25] and the SIC mechanism has been proposed as that the short chain between network junctions is firstly fully stretched to act as an oriented nucleus, and then the surrounding coiled chains partially align parallel to the nucleus to form a highly oriented crystallite.^[19,26] Meanwhile, the SIC thermodynamics proves that either larger network density or larger strain can promote SIC.^[27,28] These works provide important basis for us to investigate the natural network and structural inhomogeneity in unvulcanized NR, which is probably a key factor to shed light on why the superior properties of NR cannot be fully replicated by IR.

In this work, by combining techniques including proton double-quantum NMR tests, synchrotron small angle X-ray scattering analysis, and synchrotron wide angle X-ray scattering analysis with stearic acid (SA) as a probe, we are able to decipher the network structure from microscale to mesoscale for unvulcanized NR. We find that although the network is homogenous on microscale, it is inhomogeneous on mesoscale. This inhomogeneous structure leads to local deformation inhomogeneity, which we believe is the basic reason why unvulcanized NR shows smaller onset strain of SIC than Gel (the gel component of NR with higher network density) and even vulcanized NR do. The knowledge learned from unvulcanized NR may inspire us to design synthetic rubber networks with significantly improved mechanical properties.

EXPERIMENTAL

Sample Preparation

Natural rubber latex used in this study was fresh field latex provided by the Thai Rubber Latex Co., Thailand. The fresh latex was preserved with 0.6 vol% NH_3 at room temperature for 3 months. The latex was centrifugated at a speed of 10000 r/min for 40 min to remove sludge and water soluble impurities. The cream fraction was collected and dried in a vacuum oven at 40 °C for 2 days. The solid natural rubber was then dissolved in toluene at a concentration of 0.02 g/mL for one week.

To prepare unvulcanized NR, the toluene solution was cast onto petri dishes and dried to form films of ~1 mm in thickness.

To prepare Gel, the toluene solution was separated into heavy part and light part by centrifugation (10000 r/min, 30 min). The light part was the Sol phase that was composed of toluene-soluble rubber fraction and natural components. The heavier part was the Gel phase that contained insoluble rubber fraction and natural impurities.^[10] The collected Gel phase was then cast on petri dishes to form films of ~1 mm in thickness.

To introduce stearic acid crystallites into unvulcanized NR, the solid natural rubber was mixed with 2 phr (part per hundred rubber by weight) stearic acid on a two-roll mill.

The mixture was subjected to heat-pressing at 155 °C in a mold for 25 min to give a film of 1 mm in thickness.

To introduce stearic acid crystallites into peroxide-vulcanized natural rubber (PV-NR), the solid natural rubber was mixed with 2 phr stearic acid and 2 phr dicumyl peroxide on a two-roll mill. The mixture was cross-linked by heat-pressing at 155 °C in a mold for 25 min to give a peroxide-vulcanized natural rubber sheet of 1 mm in thickness.

In Situ Tensile X-ray Measurement

Synchrotron X-ray measurements were carried out at the beamline BL16B1 in Shanghai Synchrotron Radiation Facility (SSRF), Shanghai, China. The X-ray wavelength was 0.124 nm. A homemade mechanical stretching machine was used for symmetric deformation of rubber films (30 mm × 8 mm × 1 mm) at room temperature with a drawing speed of 6.4 mm/min and an initial length of 8 mm. The corresponding stress-strain curves were recorded by an Instron 5567 material testing machine. Two-dimensional (2D) wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) patterns were acquired using a MAR-CCD detector. The acquisition time for each frame was 30 s with an exposure time of 20 s. Aluminum oxide (Al_2O_3) and silver behenate ($\text{AgC}_{22}\text{H}_{43}\text{O}_2$) standards were used to calibrate the scattering angle for WAXD and SAXS, respectively. The sample-to-detector distances for WAXD and SAXS were 125 and 5020 mm, respectively. All diffraction and scattering signals were corrected for beam fluctuation and background scattering.^[7,29,30] X-ray data analysis was performed using the Fit2D software.

¹H Double-quantum Solid-state NMR Measurement

¹H DQ NMR measurements were performed on a Bruker advance III 300M solid-state NMR spectrometer operating at a Larmor frequency of 300.2 MHz. All experiments were conducted under static condition in a 4 mm MAS probe using 90° pulses of 3 μs. Rubber films of 10 mm × 1 mm × 1 mm uniaxially stretched to a prescribed tensile strain ($\lambda = 0$ and $\lambda = 2.0$) were wound on I-shape Teflon molds.^[31] Then the molds were centered in 4 mm o.d. MAS rotors using Teflon spacers and sealed with polyimide caps. The sample temperature was regulated at (50 ± 0.1) °C, and the rotors were prevented from spinning using Teflon-tape wrapping around the drive turbines. Finally, the pulse of Saalwachter's NMR sequence was used to collect the DQ buildup signals (I_{DQ}) and the reference decay (I_{ref}) signals of the samples with respect to the DQ evolution time (τ_{DQ}) for further data analysis.^[32] It should be pointed out that, for the strained samples ($\lambda = 2.0$), we did not adopt the accurate artificial powder method to eliminate the anisotropic effect of strained samples, considering the fact that approximation estimation is enough in the scope of the present work.^[31,33–36]

WAXD Data Analysis

In a WAXD pattern of rubber, the amorphous scattering halo comes from liquid-like short-range interference between constitutional units or chain segments, which becomes anisotropic under elongation with more intensity in the direction perpendicular to the stretching direction. To estimate crystallinity index (X_c) and oriented amorphous index (Φ_{oa}), the

WAXD patterns are deconvoluted into crystal diffraction (the 200, 120, and 201 reflections), isotropic, and oriented amorphous peaks, as shown in Fig. 1(b).^[26,29] The isotropic peak is obtained by connecting the minimum values of scattered intensity on the azimuthal scans taken at different scattering angles, which exhibits a nearly identical feature to the WAXD pattern at strain = 0.0, and both the oriented amorphous and crystal diffraction peaks appear in the remaining pattern. All the crystal diffraction, isotropic, and oriented amorphous peaks are described by the Gaussian functions. In this way, X_c and Φ_{oa} can be calculated from the diffraction intensity data by using the following equations:

$$X_c = \sum A_c / (\sum A_c + \sum A_{oa} + \sum A_{iso}) \quad (1)$$

$$\Phi_{oa} = \sum A_{oa} / (\sum A_c + \sum A_{oa} + \sum A_{iso}) \quad (2)$$

where $\sum A_c$, $\sum A_{oa}$, and $\sum A_{iso}$ represent the integrated intensities of the crystalline, oriented, and isotropic amorphous regions, respectively.

SAXS Data Analysis

In a SAXS pattern of rubber, the scattering signal arises from inhomogeneous structures including both non-rubber scatters and denser network domains. Theoretically, the scattering

curve of SAXS pattern at strain = 0 can be separated into two components with simple well-defined physical meanings by using the following formula:^[7]

$$I(s) = I_{\text{non-rubber}}(s) + I_{\text{rubber}}(s) + I_{\text{BG}} \quad (3)$$

where $I(s)$ is scattering intensity, s is scattering vector, $I_{\text{non-rubber}}$ is signal from non-rubber scatterers like protein aggregates with sharp boundary to rubber matrix, and I_{rubber} is scattering signal from density fluctuation of rubber matrix. I_{BG} is a constant fluctuation background.

$I_{\text{non-rubber}}(s)$ is described with the Debye-Bueche function by assuming sharp boundary of scatterers:

$$I_{\text{non-rubber}}(s) = I_{\text{DB}}(0) / (1 + \xi^2 s^2) \quad (4)$$

where $I_{\text{DB}}(0)$ is a prefactor and ξ is correlation length of scatterers.

I_{rubber} is estimated by the generalized Ornstein-Zernike equation involving non-sharp boundary of scatterers:^[30]

$$I_{\text{rubber}}(s) = I_{\text{GOZ}}(0) / \{1 + [(D+1)/3]\xi^2 s^2\}^{D/2} \quad (5)$$

where $I_{\text{GOZ}}(0)$ is a prefactor, ξ is correlation length of scatterers, and D is fractal dimension. The value of D is from 2 to 3 for diffuse domains, 3 for agglomerated domains with rough surface, and 4 for compact domain with smooth surface. Note that all the fitting parameters have been well

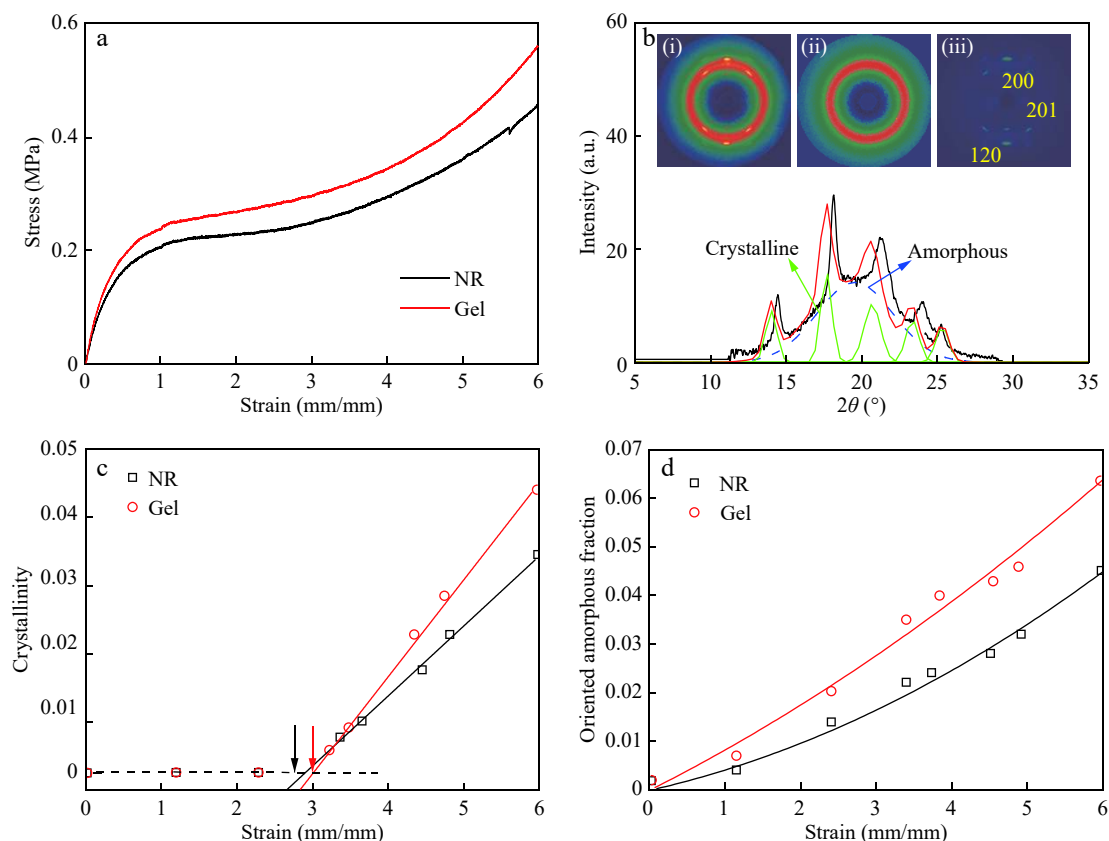


Fig. 1 Mechanical property and strain-induced crystallization of NR and Gel: (a) Stress-strain curves of NR and Gel; (b) Quantification of crystallinity index and oriented amorphous index of NR at strain = 6 by deconvoluting the WAXD pattern (i) into isotropic part (ii) and anisotropic part (iii), and the integral curve of anisotropic part (black curve) divided into crystalline peak (green curve) and oriented amorphous peak (blue dash curve) by multi-peak Gaussian fitting (red curve); (c) Crystallinity versus strain of NR and Gel, where the lines are the guide for eyes and the arrows indicate the onset of SIC; (d) Oriented amorphous fraction versus strain of NR and Gel, where the lines are the guide for eyes.

constrained in their physically reasonable ranges during the fitting process and the fitting matches well with the SAXS curves, where the values of ζ and D are expected to reflect the mesoscopic network state.

¹H DQ NMR Data Analysis

The microscopic length scale of DQ experiment is defined by the local dynamic orientational order parameter of the polymer backbone S_b , which is estimated by the residual dipolar coupling constant D_{res} of the sample and is directly related to local network density (ν) and local chain deformation:

$$S_b = \frac{3}{5N} \frac{R^2}{R_0^2} = k \frac{D_{\text{res}}}{D_{\text{static}}} \quad (6)$$

where D_{static} is static counterpart of D_{res} , R^2 is the average squared end-to-end distance of subchains between local constraints, R_0^2 is the constant, strain-independent equilibrium end-to-end distance of unstretched subchains, and N is the average number of segment of the subchains.

In an unstretched rubber network, $R^2 = R_0^2$, so

$$D_{\text{res}} \propto N^{-1} \propto \nu \quad (7)$$

As for NR,^[18,31] the relationship between the experimental D_{res} and the molecular weight between constraints M_c is

$$M_c = \frac{617 \text{ Hz}}{D_{\text{res}}/2\pi} \frac{1}{2} \text{ (kg/mol)} \quad (8)$$

Thus the distribution of D_{res} can reflect the local network density distribution.

In a stretched network, N is constant, so

$$D_{\text{res}} \propto R^2 \quad (9)$$

Thus the distribution of D_{res} can reflect the local deformation state of subchains.^[31,34]

Finally, the distribution of D_{res} in a rubber network can be estimated by Tikhonov regularization fit of the corresponding normalized DQ buildup data I_{nDQ} versus DQ evolution time τ_{DQ} ,^[18,33,34] as shown in Fig. 2(a). I_{nDQ} is obtained by a normalization procedure using two sets of experimental data I_{DQ} and I_{ref} :^[18,32,33,35]

$$I_{\text{nDQ}} = I_{\text{DQ}} / (I_{\text{ref}} + I_{\text{DQ}} - I_{\text{def}}) \quad (10)$$

where I_{def} is the exponential long-time signal tails related to network defects and is calculated by fitting the signal difference $I_{\text{ref}} - I_{\text{DQ}}$ with a decaying exponential:

$$I_{\text{def}} = A \exp(-\tau_{\text{DQ}}/T_2) \quad (11)$$

where A and T_2 are constants obtained by the fit on the long-time dependence of $I_{\text{ref}} - I_{\text{DQ}}$.

RESULTS AND DISCUSSION

Comparison of SIC Behavior between NR and Gel

Natural rubber (NR) is not completely soluble in toluene due to the presence of gel fraction (Gel). This is attributed to the existence of naturally occurring network, which limits the diffusion of most chains except those freely diffused linear chains.^[3,10] We obtained Gel from NR by centrifugation, and examined the different mechanical properties between NR and Gel using tensile test. Clearly, Gel exhibits higher tensile

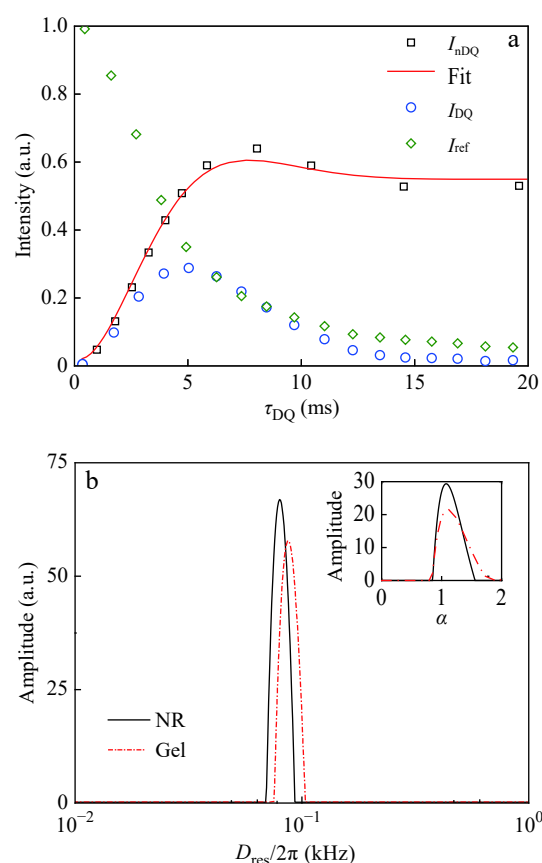


Fig. 2 Subchain length distribution of NR and Gel: (a) Calculation of residual dipolar coupling constant D_{res} of NR at strain = 0 by Tikhonov regularization fit^[33] (red line) of the normalized double-quantum (DQ) NMR signal I_{nDQ} with respect to the evolution time τ_{DQ} , where I_{nDQ} is obtained by a normalization procedure using two sets of experimental data I_{DQ} and I_{ref} (see details in Experimental Section); (b) D_{res} distribution of NR and Gel at strain = 0, where D_{res} at strain = 0 is inversely proportional to the average number of chain segments between local constraints; the inset is the distribution of chain deformation ratio α of NR and Gel at strain = 2, where α is defined as $D_{\text{res}}(\text{strain} = 2)/\bar{D}_{\text{res}}(\text{strain} = 0)$, $D_{\text{res}}(\text{strain} = 2)$ is D_{res} at strain = 2 and is proportional to the average squared chain end-to-end distance between local constraints, and $\bar{D}_{\text{res}}(\text{strain} = 0)$ is a constant corresponding to the mean value of D_{res} at strain = 0.

strength than NR due to its higher network density, as shown in Fig. 1(a). During the tensile tests, *in situ* synchrotron X-ray measurements were carried out to probe SIC for both NR and Gel. The crystallinity index (X_c) and oriented amorphous index (Φ_{oa}) can be quantified using profiles in Fig. 1(b) (see details in Experimental Section). By plotting X_c versus strain, we can define the onset strain of SIC as the intersection point of linear fitting lines, as shown in Fig. 1(c). Interestingly, NR shows smaller onset strain of SIC than Gel does ($\epsilon_{\text{onset}} = 2.7$ for NR and 3 for Gel), despite that NR shows lower mechanical property and slower crystallization rate which can be derived from the slope of the lines in Fig. 1(c) due to its smaller network density. Furthermore, by plotting Φ_{oa} versus strain, we find that the fraction of oriented amorphous chain in NR is always smaller than that in Gel in the whole stretching process, as shown in Fig. 1(d). Since the oriented

chain segments are induced by local chain elongation along the stretching direction, this result suggests the average strain of local chains in NR is smaller along stretching direction, given the same macroscopic strain in both NR and Gel. Here it is very interesting to observe the conflict that NR has smaller fraction of oriented chain segments in the whole stretching process but shows smaller onset strain of SIC than Gel does.

Comparison of Subchain Length between NR and Gel

Since SIC is closely related to the evolution of microscopic structure during stretching, some basic understanding about the microscopic state of the strained or unstrained networks should be established. For this purpose, proton double-quantum (DQ) NMR method is used to probe the statistical distribution of chain end-to-end distance in a strained or unstrained entanglement network (see detailed analysis in Experimental Section). At first, we can obtain the distribution of residual dipolar coupling constant D_{res} of the network using profiles in Fig. 2(a) (see details in Experimental Section). Theoretically, in an unstrained network D_{res} is inversely proportional to the average number of chain segments between local constraints and thus proportional to local network density, while in a stretched network D_{res} is proportional to the average squared chain end-to-end distance between local constraints.^[31] Therefore, the distribution of D_{res} is a useful microscopic state index to reflect statistical distribution of subchain length between constraints. Compared with Gel, the mean value of D_{res} in NR is smaller, as shown in Fig. 2(b), suggesting that NR has smaller local network density, which is the reason why the tensile stress of NR is smaller than that of Gel (Fig. 1a). Moreover, both NR and Gel have very narrow distribution of D_{res} , which reflects that both NR and Gel are basically homogeneous at chain length scale, since the narrow distribution of D_{res} means the narrow distribution of subchain length between constraints. If we stretch both samples to a strain = 2.0, the distribution of D_{res} becomes slightly wider due to the increased end-to-end distance of strained chains for both NR and Gel, as shown in the upper inset of Fig. 2(b), but most chains remain unstretched or just slightly stretched and the average chain deformation ratio α is small. Here, α is defined as $D_{\text{res}}(\text{strain} = 2)/\bar{D}_{\text{res}}(\text{strain} = 0)$, where $D_{\text{res}}(\text{strain} = 2)$ is D_{res} at strain = 2 and is proportional to the average squared chain end-to-end distance between local constraints, and $\bar{D}_{\text{res}}(\text{strain} = 0)$ is a constant corresponding to the mean value of D_{res} at strain = 0. A closer observation reveals that the distribution width of stretched NR is smaller than that of Gel, suggesting that NR has a smaller fraction of elongated chains formed during stretching and the elongated chains show lower deformation ratio α , which appears to agree well with the result of Φ_{oa} obtained by WAXD in Fig. 1(d). Overall, the microscale structure revealed by DQ NMR cannot explain the reason why NR shows smaller onset strain of SIC than Gel does.

Mesoscale Structural Inhomogeneity of NR, Gel, and PV-NR

The inhomogeneity of natural network in natural rubber is usually neglected given the fact of the low network density

and the homogeneous subchain length distribution of NR. Nevertheless, due to the everlasting network density fluctuation controlled by chain relaxation dynamics, network inhomogeneity theoretically exists under different length scales as a coherent property of rubber network.^[37] Therefore, the extent of inhomogeneity in a network depends on the length scale selected by observers, and a network generally appears to be more inhomogeneous at certain length scale than at other length scales.

Here, considering the typical diameter of chain clusters that produce crystals at onset strain of SIC is around 100 nm, we choose the observation length scale as 100 nm (defined as mesoscale size) and assume that the rubber matrix is made up of numerous 100 nm-diameter chain clusters.^[11,19,22] These clusters theoretically can be distinguished as denser mesoscale domain (mesodomain) with higher network density and sparser mesodomain with lower network density, even if network density fluctuation at this mesoscale (100 nm) is very small, like what is found in peroxide-vulcanized natural rubber (PV-NR).^[18,23–25] The spatial organization of denser/sparser mesodomains would lead to some inhomogeneity pattern of the rubber structure on mesoscale, which determines the mesoscale deformation inhomogeneity and thus SIC process as well as rubber mechanics.

To estimate the mesoscale inhomogeneity pattern of NR, *in situ* synchronic small angle X-ray scattering (SAXS) patterns were recorded, as shown in Fig. 3(a). The scattering signal originates from inhomogeneous structure including both non-rubber scatters and denser network domains. The structural information of the denser network can be separated out by fitting the scattering curve of SAXS pattern at strain = 0 using Eq. (3), as shown in Fig. 3(b) (see data analysis in Experimental Section). After carefully optimizing the decomposition fitting process, we obtain the length scale index ζ and boundary sharpness index D of inhomogeneous network domains in NR, Gel, and PV-NR. It is revealed that the length scale of denser domains of NR and Gel lies on the magnitude of ~100 nm, while that of PV-NR is much smaller on the magnitude of ~10 nm approaching subchain length. This suggests that NR and Gel are inhomogeneous at mesoscale but PV-NR is relatively homogenous at the same scale. On the other hand, the inhomogeneous domains of NR show slightly higher boundary sharpness than that of Gel, suggesting that NR has larger network density contrast between denser and sparser domains than Gel. ζ and D collectively suggest that NR is more inhomogeneous than PV-NR and Gel at mesoscale. Note that our fitting result of ζ for PV-NR is in good agreement with the well-established conclusion that PV-NR is inhomogeneous at subchain length scale but has relatively homogeneous mesoscale structure and deformation, which supports the validity of our fitting process and suggests that the network density and deformation of both the denser and sparser mesodomains of PV-NR have no sharp difference.^[18,23–25]

Further, we would briefly discuss the reason of mesoscale inhomogeneity of NR from the viewpoint of network formation. First, the mesoscale homogeneity of PV-NR is derived from the random crosslinking process of peroxide vulcaniza-

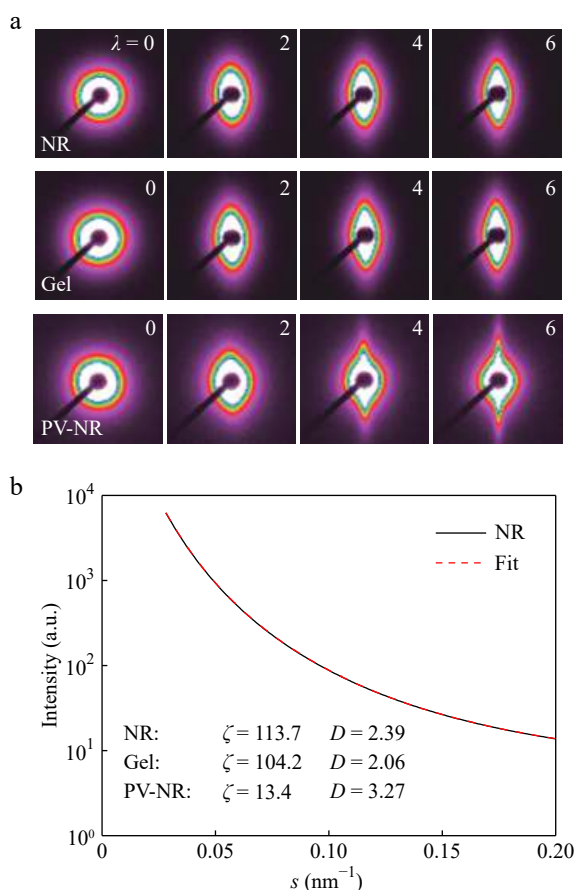


Fig. 3 Large-scale inhomogeneous structure analysis of NR, Gel, and PV-NR: (a) 2D SAXS pattern evolution with strain λ of NR (top row), Gel (middle row), and PV-NR (bottom row); (b) Fitting of 1D SAXS curve of unstretched NR (black solid line) using Eq. (3) (red dash line). Following the fitting process, ζ and D of NR, Gel, and PV-NR can be obtained correspondingly, where ζ is the correlation length of denser network domains in nanometer, and D is the fractal dimension. The value of D is from 2 to 3 for diffuse domains, 3 for agglomerated domains with rough surface, and 4 for compact domain with smooth surface.

tion,^[23] and in turn the random crosslinking results in a wide distribution of subchain length and thus PV-NR shows inhomogeneity at subchain length scale.^[18] In contrast, the mesoscale inhomogeneity of NR is supposed to mainly arise from the dynamic critical fluctuations of NR latex at the onset of gelation.^[37] Finally, Gel is obtained by centrifugation of NR solution (see Experimental Section), and the deviation of inhomogeneity features of Gel from NR is mainly controlled by different chain diffusion rates in different mesodomains during centrifugation. In detail, compared with denser mesodomains, soluble chains would be preferably removed from sparser mesodomains of NR due to its smaller topological constraints for chain separation. This separation of soluble chains would increase network density of the corresponding domains to counterbalance the density difference between all mesodomains, making Gel reasonably more homogeneous than NR at mesoscale.

Mesoscale Deformation Inhomogeneity of NR

Mesoscale structural inhomogeneity of NR would certainly

result in mesoscale deformation inhomogeneity. Next, we will focus on the mechanism of mesodomain deformation in stretched NR. During stretching, denser mesodomains would become more oriented along stretching direction, as indicated by the low- q range orientational signal of SAXS pattern in Fig. 3(a). A closer observation of these oriented SAXS patterns shows that the pattern evolution of PV-NR obviously diverges from NR and Gel in detail, suggesting some distinguishable orientation difference of denser mesodomains between NR and PV-NR, as ascribed to their quite detectable difference in mesoscale structural inhomogeneity. To further reveal their different mesodomain orientation states, a probe is applied to detect the evolution of mesodomain deformation during stretching for both NR and PV-NR.

Stearic acid (SA) is a common component in rubber vulcanization recipe. It is used as a plasticizer to enhance the molecular mobility and a reagent to tune the vulcanization rate of rubber. When cooled after the vulcanization process, SA is known to form crystal platelets of several nanometers.^[19,22,38] These crystal platelets have no chemical interaction with rubber chains, but during uniaxial deformation they can be gradually oriented along the stretching direction in response to their surrounding network deformation.^[19,22] This makes SA applicable to be a potential probe to detect mesodomain deformation in our experiments. Here, *in situ* synchrotron X-ray measurements were carried out to probe the orientation of SA crystallites in both NR and PV-NR during uniaxial stretching, and the result is shown in Fig. 4. First, the WAXD pattern of SA crystal is shown in Fig. 4(a) with clear crystal plane information, where the (003) crystal plane is a good signal for further quantifying the orientation of SA probe. Typically, the (003) plane of SA in the center of WAXD pattern at strain = 0 shows randomly oriented signal (see Fig. 4b, i and iii), while at strain = 6 the highly oriented signal of SA crystallites can be observed (see Fig. 4b, ii and iv). The orientation of SA crystallites is quantified by orientational order parameter $\langle \overline{P}_2 \rangle$, which has a value from 0 to 1, where 0 and 1 correspond to an isotropic structure and a perfect orientation along the stretching direction, respectively.^[22] To calculate $\langle \overline{P}_2 \rangle$, the azimuthal intensity distribution of 003 reflection is acquired and fitted to a Maier-Saupe distribution function (see Fig. 4b, v):

$$I = I_0 + A e^{\beta \cos^2(\phi - \phi_0)} \quad (12)$$

where I_0 denotes the free baseline intensity, ϕ_0 is the azimuth at the position of the maximal intensity, ϕ is the azimuth, and β is a parameter that determines the width of the distribution. Subsequently, $\langle \overline{P}_2 \rangle$ can be determined using the formula:

$$\langle \overline{P}_2 \rangle = \frac{\int_{-1}^1 P_2(\cos\phi) e^{\beta \cos^2\phi} d\cos\phi}{\int_{-1}^1 e^{\beta \cos^2\phi} d\cos\phi} \quad (13)$$

where $P_2(\cos\phi) = \frac{1}{2}(3\cos^2\phi - 1)$.

By plotting $\langle \overline{P}_2 \rangle$ versus strain, it is interesting that NR shows higher orientation of SA crystallites than PV-NR does under all the strains, as shown in Fig. 4(c). Considering that SA orientation is induced by the surrounding mesodomain

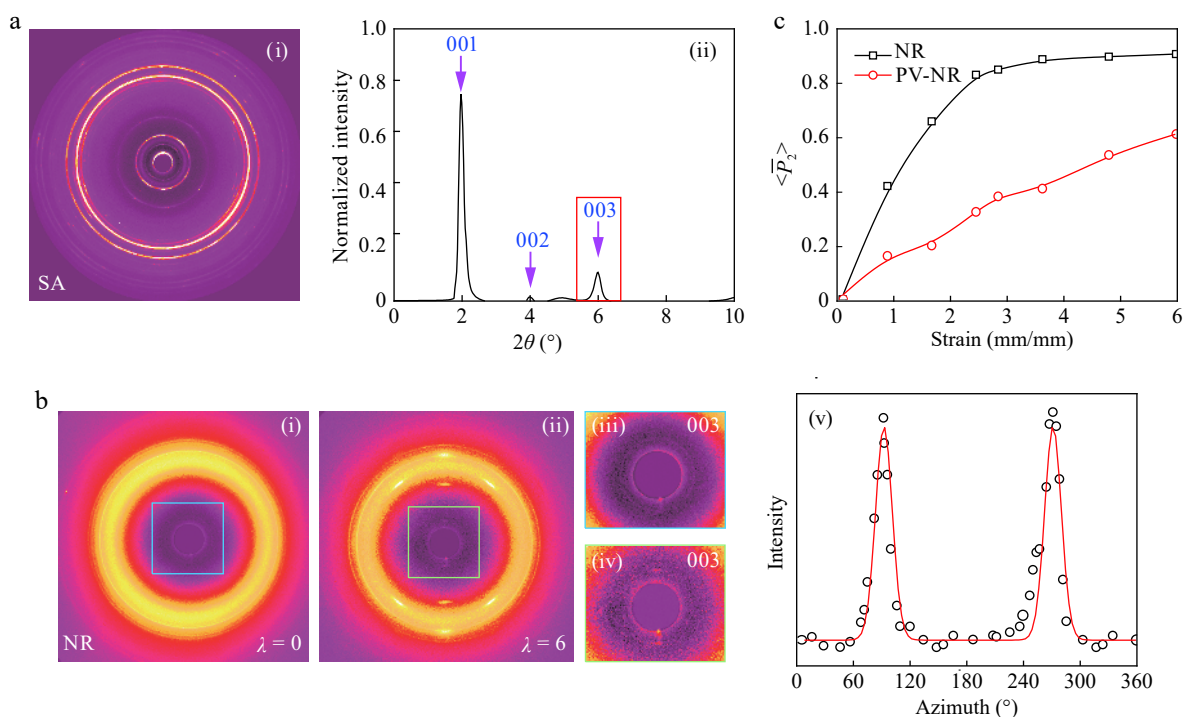


Fig. 4 Stearic acid (SA) probe orientation analysis of NR and PV-NR: (a) WAXD pattern of SA crystal (i) and the crystal planes in 1D WAXD curve (ii); (b) WAXD patterns of NR at strain = 0 (i) and strain = 6 (ii), with the corresponding enlarged WAXD pattern center given in (iii) and (iv), respectively, where the (003) plane of SA is isotropic at strain = 0 (iii) and becomes highly oriented at strain = 6 (iv), and this orientation is quantified by fitting azimuthal intensity distribution of SA's (003) plane (v) using Eq. (12); (c) Orientational order parameter $\langle P_2 \rangle$ of SA's (003) plane versus strain of NR and PV-NR, where the lines are the guide for eyes; $\langle P_2 \rangle = 0$ and $\langle P_2 \rangle = 1$ correspond to the isotropic structure and the perfect orientation along the stretching direction, respectively, and the increase of $\langle P_2 \rangle$ from 0 to 1 indicates a transformation from disorder to order.

deformation, the higher orientation of SA crystallites basically reflects that NR has some mesodomains with much larger orientation degree.

This finding provides a linkage between the earlier SIC behavior of NR and its inhomogeneous deformation on meso-scale. These highly oriented mesodomains in NR are supposed to be responsible for its smaller onset strain of SIC when compared with Gel and even PV-NR. Here we compare both the SIC behavior and the subchain length between NR and PV-NR, as shown in Fig. 5. Note that NR in Figs. 4 and 5 is prepared by hot press (instead of solution-casting samples used above) to ensure similar preparation process between NR and PV-NR. Expectedly, it is revealed that NR shows much lower tensile strength (see Fig. 5a, i) and smaller oriented amorphous fraction Φ_{oa} (see Fig. 5a, ii) due to its much lower network density, and that PV-NR shows relatively wide subchain length distribution in both strained and unstrained states (see Figs. 5b, i and ii). However, it is very interesting that NR still shows smaller onset strain of SIC (see Fig. 5a, iii), similar to Fig. 1(c). This phenomenon in turn validates the similarity between Gel and PV-NR: both of them have relatively homogenous structure and deformation on mesoscale compared to NR.

Linking Mesoscale Deformation to Subchain Deformation

Now we focus on elucidating the subchain deformation sce-

nario of NR under the context of mesoscale deformation inhomogeneity. Considering SIC of NR is known as a transformation process from the disordered state to the ordered state of chain segment alignment along the stretching direction,^[19,27,28] here we define a quantity “orientational strain γ ” of subchain—the ratio between the fraction of oriented chain segment in the strained and unstrained state of the subchain, as shown in Fig. 6(a), where the orientational strain γ can be expressed as $\gamma = (R'_z - R_z)/R_z$ with z axis being the stretching direction; the deformed chain end-to-end vector is marked as $R' = (R'_x, R'_y, R'_z)$ and its original state at strain = 0 is marked as $R = (R_x, R_y, R_z)$. In other words, γ is the local strain of subchain along the stretching direction, which is a more direct quantity than the macroscopic strain or the subchain end-to-end deformation to promote the oriented amorphous fraction Φ_{oa} and the crystal formation. In detail, the orientational strain γ can be used to explain why the small chain deformation ratio α of NR and Gel (see Fig. 2b) could lead to earlier SIC behavior: the subchains prefer to be oriented during stretching rather than to change the end-to-end distance (the distance between the two terminals of the chain), which is the case for weakly cross-linked network as described by a tube model in previous studies,^[31,39,40] thus NR and Gel could have small α but large γ to promote SIC.

Following this analysis, the orientational strain γ of subchain is then used to describe the subchain deformation of mesoscale inhomogeneous network. As mentioned before,

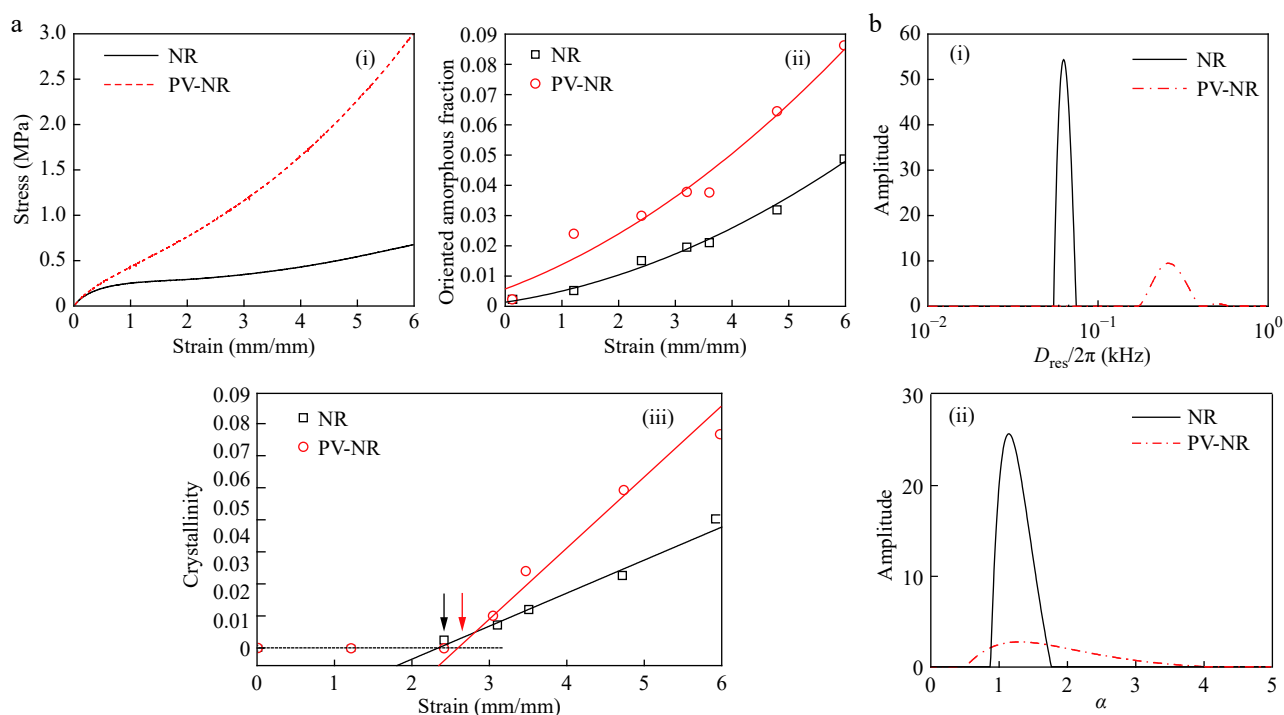


Fig. 5 Comparison of (a) SIC behavior and (b) subchain length distribution between NR and PV-NR: (a) stress (i), oriented amorphous fraction (ii), and crystallinity (iii) versus strain, where the lines in (ii) and (iii) are the guide for eyes and the arrows in (iii) indicate the onset of SIC; (b) D_{res} distribution at strain = 0 (i) and α distribution at strain = 2 (ii)

considering the typical diameter of chain clusters that produce crystals at onset strain of SIC is around 100 nm,^[11,19,22] we assume here that the rubber matrix is made up of numerous 100 nm-diameter chain clusters, and that these clusters theoretically can be distinguished as denser mesodomains with higher network density and sparser mesodomains with lower network density, even if the network density fluctuation at this mesoscale (100 nm) is very small. This mesoscale rubber structure is visualized in the upper (strained state of rubber clusters)/bottom (unstrained state of rubber clusters) insets of Fig. 6(b), where the red threads inside clusters represent the overall chain orientation/deformation states. The organization of denser/sparser mesodomains would lead to some inhomogeneity pattern of the rubber structure at mesoscale, which determines the mesoscale deformation inhomogeneity and thus SIC process as well as rubber mechanics.

Based on this mesoscale rubber structure, we define that the average γ of the whole matrix as well as the denser and sparser mesodomains are γ_{matrix} , γ_{denser} , and $\gamma_{sparser}$, respectively. Since denser and sparser mesodomains are alternatively distributed in the whole matrix as the result of network density fluctuation, we deduce here that denser mesodomains can form a percolated network which sustains most of stress transferred from rubber matrix. Also, the denser mesodomains would have lower chain relaxation rate under stress due to its higher network density. Thus, the denser domains have larger average γ than the sparser domains do during deformation, which is responsible for the onset of SIC. Collectively, there exists the relationship $\gamma_{denser} > \gamma_{matrix} > \gamma_{sparser}$ given a macroscopic strain, as shown in Fig. 6(b).

Finally, analyzing the orientational strain γ of subchain could reveal the underlying picture controlling the onset strain of NR, Gel, and PV-NR. Since the network density of NR is smaller, its smaller onset strain of SIC suggests that it has larger γ_{denser} than Gel and PV-NR. On the other hand, NR shows smaller oriented amorphous fraction Φ_{oa} than Gel and PV-NR do at equal macroscopic strain, which suggests that NR has smaller γ_{matrix} . To address this dilemma, it is deduced that $\gamma_{denser}^{NR} > \gamma_{denser}^{Gel} > \gamma_{matrix}^{Gel} > \gamma_{matrix}^{NR} > (\gamma_{sparser}^{Gel}) > \gamma_{sparser}^{NR}$ given a macroscopic strain (see Fig. 6c). As for PV-NR, the network density and deformation of both the denser and sparser mesodomains have no obvious difference and $\gamma_{denser}^{PV-NR} \cong \gamma_{matrix}^{PV-NR} \cong \gamma_{sparser}^{PV-NR}$. Under the equal macroscopic strain of NR and PV-NR, $\gamma_{denser}^{NR} > \gamma_{denser}^{PV-NR} > \gamma_{matrix}^{PV-NR} > \gamma_{matrix}^{NR} > (\gamma_{sparser}^{PV-NR}) > \gamma_{sparser}^{NR}$ (see Fig. 6c). These comparison relationships of subchain deformation in Fig. 6(c) elucidates the underlying reason why NR shows smaller onset strain of SIC and reveals the mechanism behind natural network promoting SIC, that is, the inhomogeneous orientational strain of subchains.

CONCLUSIONS

To summarize, compared with Gel and PV-NR, NR possesses smaller fraction of oriented chain segments during stretching but shows smaller onset strain of SIC; in contrast with its SIC behavior, NR also shows very small average chain deformation ratio α . To address this dilemma, the concept “orientational strain γ ” is introduced to illustrate that NR could have small α but large γ to promote SIC; the mesoscale rubber structure is described by an approximation that the

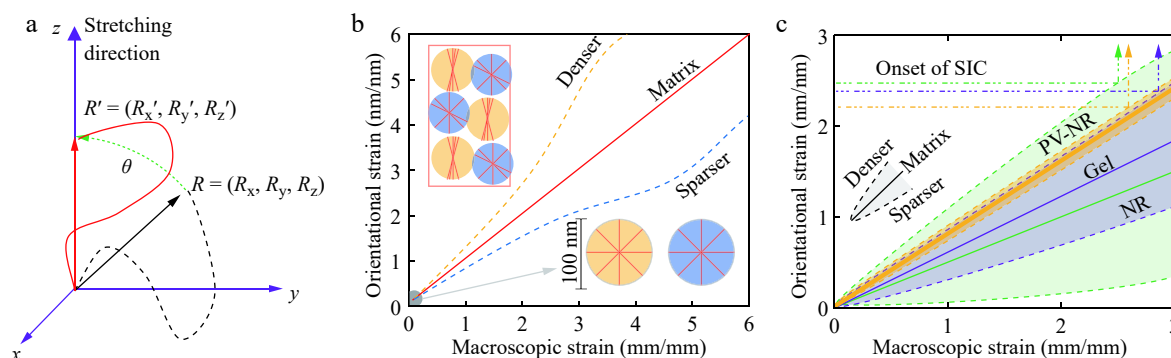


Fig. 6 Illustration of orientational strain γ versus macroscopic strain of NR, Gel, and PV-NR: (a) Typical chain deformation of NR under macroscopic strain = 2, where the end-to-end vector R at strain = 0 (black arrow) is changed to R' at strain = 2 (red arrow) by rotating an angle θ (green arrow) to the stretching direction with little elongation; the orientational strain γ is defined as the chain elongation along the stretching direction (z axis) and is calculated here as $\gamma = (R'_z - R_z)/R_z$, which contributes to the formation of an ordered/oriented network and the onset of strain-induced crystallization (SIC); (b) The conceptual evolution of average chain orientational strain γ per 100 nm-diameter chain cluster (distinguished as denser (gold dash line) and sparser (blue dash line) mesodomain) with respect to the macroscopic strain of a conceptual network matrix (red solid line), where the red solid line represents the average γ of the whole matrix that is assumed to be equal to the macroscopic strain; the bottom inset is an illustration of a 100 nm-diameter denser (gold) and sparser (blue) mesodomain at macroscopic strain = 0 with random chain orientation (uniform distribute red strands); the upper inset is an illustration of chain orientation (oriented red strands) of the denser/sparser mesodomains in the matrix (red rectangle) under macroscopic strain = 2, where the denser mesodomains show higher γ ; (c) A proposed evolution of γ of the matrix (solid line), denser mesodomain (upper dash line around shadow), and sparser mesodomain (bottom dash line around shadow) versus macroscopic strain of NR (green), Gel (purple), and PV-NR (gold), where PV-NR is a mesoscale homogenous network that shows little γ difference between denser and sparser mesodomains but the largest γ of matrix during deformation, and NR shows the largest γ difference between denser and sparser mesodomains but the smallest γ of matrix; the arrows indicate the correlation between the onset strain of SIC and the γ of denser mesodomain.

rubber matrix can theoretically be the alternating structure of denser and sparser mesodomains of 100 nm-diameter. Importantly, the claim has been established that NR has more inhomogeneous mesoscale (~100 nm) structure and deformation than Gel and PV-NR do, and more specifically, the average γ in sparser mesodomains of NR is smaller but the denser mesodomains of NR can reach larger average γ than each area of Gel and PV-NR, which elucidate the reason why NR shows smaller onset strain of SIC and reveals the underlying mechanism of how natural network promotes SIC. Overall, the present work constructs an initial mesoscale model of NR to describe the inhomogeneous natural structure and deformation, revealing a precious lesson from the nature to approach high-performance rubber structures at meso-scale, and potentially sketching a route to investigate the inhomogeneity and deformation from simple to complex networks.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 51333003) and Special Fund for Agro-scientific Research in the Public Interest (No. 201403066-1).

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