

REVIEW

Features of strain-induced crystallization of natural rubber revealed by experiments and simulations

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Understanding the strain-induced crystallization (SIC) mechanism of natural rubber (NR) is a prerequisite for comprehending the reinforcement mechanism of NR and for designing new high-performance rubber materials. With the help of new technologies that have enabled more accurate experimental measurement of the microstructure and the use of molecular simulations that can be applied to probe structural changes during stretching in real time, some interesting results have been found. For instance, even at high strains, a very large fraction of the unoriented amorphous phase still remains in the stretched sample with homogeneous or heterogeneous networks. In addition, the onset strain of SIC in peroxide-cured NR decreases with an increasing crosslinking density, while sulfur-cured NR is independent of the crosslinking density, which cannot be explained by conventional theories. The presence of nanofillers, entanglements, non-rubber components and pseudoend-linked networks also results in abnormal phenomena of SIC.

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INTRODUCTION

Rubber is an indispensable raw material due to its high elasticity. Several types of rubber can crystallize when exposed to external stretching,^{1–4} such as natural rubber (NR), polychloroprene rubber and polyisoprene rubber (IR). Strain-induced crystallization (SIC) behavior endows these rubbers with excellent mechanical properties and good resistance to crack growth. To help researchers to understand the structure–property relationships in rubber materials, many studies have been conducted to investigate the process of SIC at a microscopic level.

The SIC of rubber is an ‘old’ subject. Even before Staudinger⁵ proposed the concept of macromolecules, the British philosopher Gough⁶ reported that his lips sensed warmth while stretching NR. The warmth sensed by Gough was mainly derived from the latent heat released by SIC rather than because of changes to the conformational entropy of NR, since the latent heat raises the temperature by up to 10 K at 500% strain, while the adiabatic loss of conformational entropy can only reach 1 K if extrapolated from 100 to 500% strain, based on the experimental data in Treloar’s book on rubber elasticity.⁷ In 1925, Katz⁸ directly observed stretched NR crystallizing at room temperature based on the measurements of wide-angle X-ray diffraction (WAXD). Since then, many SIC studies of NR have been conducted using WAXD, infrared dichroism and birefringence measurements.^{4,9–13} In addition, transmission electron microscopy studies have revealed that rubber crystals exhibit different crystalline morphologies at different strains (spherulites at low strains, shish-kebab structures at intermediate strains and fibrous crystallites at high strains).^{14–16} Flory¹⁷ is thought to be the first person to predict that the entropic loss of stretched rubber chains results in an increased

melting point, and thus favors crystallization from a thermodynamic point of view.

Recently, due to the development of some new technologies that have enabled more accurate experimental measurement of the microstructure and the use of molecular simulations, the microstructural changes of crystallizable rubber during deformation can be directly studied in real time. For instance, *in situ* synchrotron WAXD is one of the mature technologies that can be used to probe the SIC process of rubber.^{18–24} When using conventional in-laboratory X-ray technology, researchers must stop stretching the rubber and hold the sample still during measurements. When stretching is stopped, the stress is relaxed and the microstructures may change. These changes may affect the experimental results. However, synchrotron WAXD has a very high intensity, and can be used to observe crystallization behavior in real time. The use of synchrotron WAXD has revealed some results that have been inconsistent with conventional ideas and theories.^{20,24} In addition to experiments, molecular simulation has recently become a powerful method for directly probing molecular structures and motions.^{25–28} Subsequently, more details of microstructural evolution during stretching have been successfully observed based on molecular simulations.^{29–32} Thus, the SIC of rubber has become a ‘new’ subject. In the following sections we introduce the new findings and discuss several key factors controlling the behaviors of SIC of NR, which differ from the former reviews^{33–36} of SIC of NR.

STRETCH-INDUCED STRUCTURAL CHANGES IN CROSSLINKED NR

The conventional theories of rubber elasticity assume that all amorphous chains are deformed or oriented gradually during

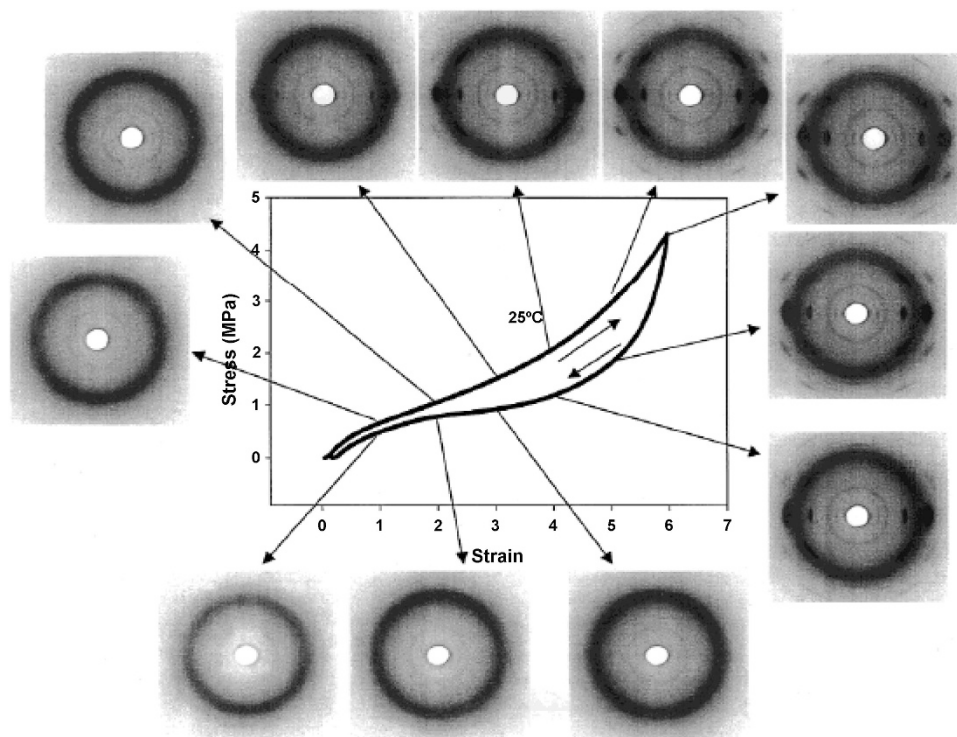


Figure 1 Stress–strain relationship and selected WAXD patterns collected during stretching and relaxation of natural rubber. Reprinted with permission from Toki *et al.*²⁰ Copyright (2002) American Chemical Society.

deformation. However, using *in situ* synchrotron WAXD (as seen in Figure 1), Toki *et al.*^{20,24} showed that even at high strains a very large fraction of the unoriented amorphous phase remained, while only a small fraction of oriented amorphous chains existed in the stretched rubber. They attributed this abnormal phenomenon to the nonhomogeneous distribution of the crosslinked network points.^{20,24} During stretching, the network chains with short-chain lengths between the dense crosslinking points can become oriented and form crystallites, while the network chains with much longer chain lengths remain in the random coil state. Further investigations showed that peroxide crosslinked NR (P-NR), which is assumed to possess a more homogeneous random network structure relative to sulfur-cured NR (S-NR),³⁷ also exhibited only a small fraction of the oriented amorphous phase at high strains.^{37,38} In other words, there may be another explanation for the small fraction of oriented amorphous chains in stretched rubber.

Lately, Hu's group performed dynamic Monte Carlo simulations to investigate the SIC of polymer networks with a uniform distribution, and they also found that amorphous bonds have low orientational orders during stretching,³¹ as shown in Figure 2. Namely, the distribution of crosslinked network points should not be the main origin of the low fraction of oriented amorphous segments at high strains. Furthermore, their simulation findings revealed that although all the network chains with a homogeneous distribution as a whole are uniformly deformed, the short segments along each chain still contain various degrees of stretching.³¹ Then, during stretching, some short segments with a high orientation initiate crystal nucleation, while the less stretched segments participate in crystal growth with more chain-folding.³¹ These results are distinctly different from conventional ideas, which assume that network chains with a uniform distribution should have the same degree of deformation.

Stretching can cause rubber chains to orientate, which may further influence the crystal nucleation mechanism. Hu's group employed dynamic Monte Carlo simulations to reveal the effect of homogeneous stretching on the crystal nucleation of polymer networks.²⁹ They found that the probability of chain-folding in newly emerging crystallites suddenly decreases beyond a critical strain and that this is correlated with a possible transition from the formation of chain-folding nuclei to fringed-micelle nuclei. Therefore, at low strains, chain-folded nuclei are formed, while above the critical strain, the formation of fringed-micelle nuclei is favored. Figure 3a comparatively depicts the onset strain of crystallization and the critical strain for the formation of fringed-micelle nuclei at different temperatures. Two regions with different dominating nucleation mechanisms can be observed. At low temperatures ($T < 4.0$), the critical strains are higher than the corresponding onset strains. That is, at low temperatures, crystal nucleation occurs mainly through the formation of chain-folded nuclei. When the strain increases to a critical value, a nucleation mechanism transition from folded-chain nuclei to fringed-micelle nuclei occurs. At high temperatures ($T > 4.0$), the critical strains coincide with the onset ones, indicating that nucleation of fringed-micelles is preferred. This nucleation mechanism transition can be predicted by the competition between the free energy barriers for the two nucleation mechanisms according to the classical nucleation theory.^{29,39,40}

Further investigations have revealed that there are other factors that also influence the nucleation process during stretching. Using synchrotron WAXD, Liu *et al.*⁴¹ found that self-seeding can increase the critical strain of the nucleation mechanism transition and that the onset strain is simultaneously reduced. They introduced residual temperature-induced crystallization-melting crystallites into a rubber sample. At the early stretching stage, the formation of low-oriented crystals was observed. These low-oriented crystals are formed by

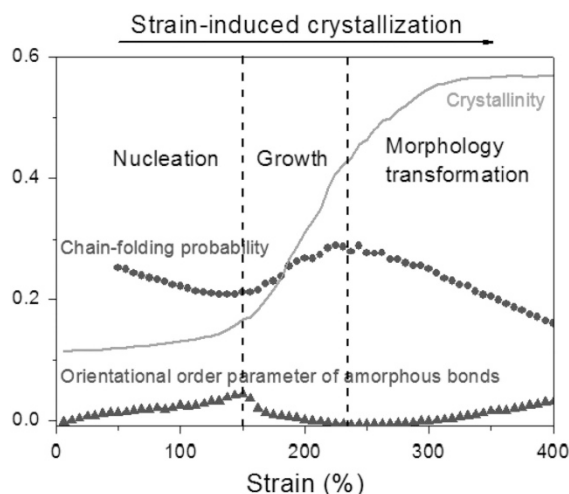


Figure 2 Strain–evolution curves showing the orientational order parameters of crystalline bonds and amorphous bonds, the chain-folding probability of crystals and crystallinity at a reduced temperature of 4.5. Reprinted with permission from Nie *et al.*³¹ Copyright (2014) Elsevier. A full color version of this figure is available at *Polymer Journal* online.

folded-chain nucleation on the surface of unoriented residual temperature-induced crystallization-melting crystallites (self-seeding). Further stretching results in the appearance of highly oriented crystals due to the fringed-micelle nucleation and the rotation of previously low-oriented crystals along the stretching direction. With the help of self-seeding, Liu *et al.*²⁹ successfully illustrated the occurrence of a nucleation mechanism transition from folded-chain nucleation to fringed-micelle nucleation during SIC of NR, validating the simulation findings of Hu's group.

NETWORK STRUCTURE OF CROSSLINKED NR

With the help of the synchrotron WAXD technique, Tosaka and colleagues^{42,43} observed another phenomenon that is inconsistent with the conventional theory. According to the classical theory of rubber elasticity,^{7,17,44,45} all the network chains were assumed to have the same chain length. The reduction of conformational entropy that directly dominates the onset of SIC is dependent on the crosslinking density, and thus the onset strain should depend on the crosslinking density. Surprisingly, Tosaka and colleagues^{42,43} detected that the onset strain for S-NR is almost independent from the crosslinking density. They attributed this special phenomenon to inhomogeneous deformation due to the inhomogeneous topology of chains. Nevertheless, for P-NR, the stretching ratio at the onset of SIC decreases with increasing crosslinking density.^{37,38} The different behaviors of SIC between P-NR and S-NR may be caused by the different network structures of these two types of rubbers. Therefore, the network structure of S-NR is thought to be less homogeneous compared with that of P-NR.³⁷ On the basis of some experimental studies,^{46,47} Ikeda *et al.*³⁷ proposed a two-phase model of a heterogeneous network structure for S-NR, in which domains of high crosslinking density are embedded in a rubbery network matrix with low crosslinking density, as illustrated in Figure 4. The formation of the domain with higher crosslinking density is attributed to the active sulfur crosslinking reactions in the presence of sulfur around zinc oxide particles.³⁷ They further noted that SIC mainly occurs in the rubbery matrix with low crosslinking density, while the domains of high crosslinking density act as reinforcing fillers. An increase in the fraction of sulfur can only lead to an increase in the crosslinking

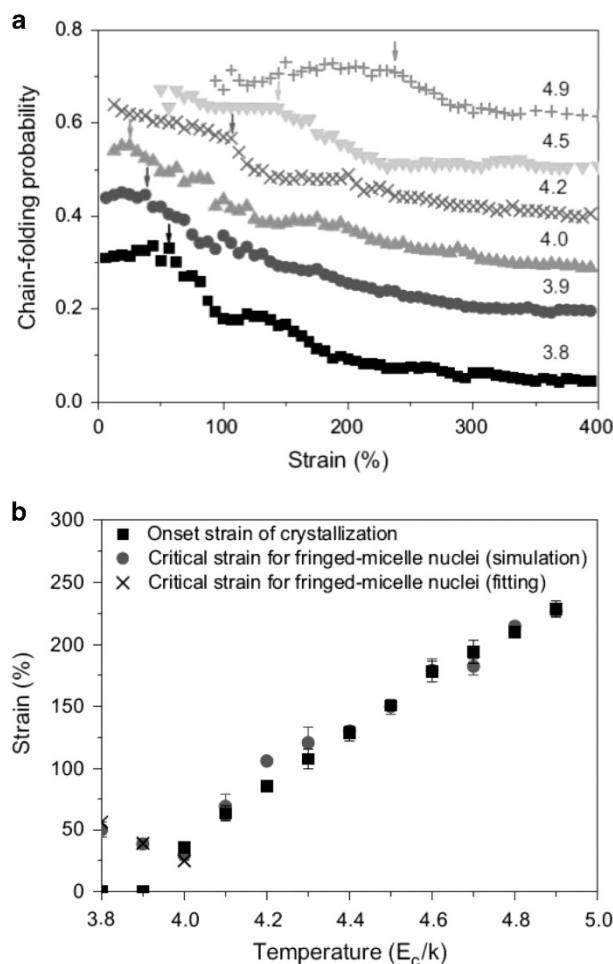


Figure 3 (a) Evolution of the chain-folding probability with increasing strain in small crystallites emerging during stretching at various temperatures. For clarity, the six curves are vertically shifted (from bottom to top) by 0, 0.15, 0.25, 0.35, 0.45 and 0.55, respectively. The arrows indicate the strain where the formation of fringed-micelle nuclei was preferred due to stretching. (b) Comparison between the onset strains of crystallization and the critical strains for the formation of fringed-micelle nuclei at various temperatures. Reprinted with permission from Nie *et al.*²⁹ Copyright (2013) Elsevier. A full color version of this figure is available at *Polymer Journal* online.

density in the high crosslinking density domain, while the crosslinking density in the low crosslinking density domain is nearly constant. Thus, an increase in the overall crosslinking density could not induce the changes of the onset strain.

To confirm their two-phase network structure model, Ikeda's group investigated the microscopic structures of P-NR and S-NR by performing small-angle neutron scattering measurements.^{48,49} They successfully detected the existence of a dense network domain with a characteristic length of 10–100 nm in S-NR, thus validating their two-phase network structure model. The network inhomogeneities of P-NR were strongly suppressed by the addition of dicumyl peroxide. However, the controversy still continues. Tosaka⁵⁰ proposed a different network structure model for the thermodynamic description of SIC. He assumed that the crosslinked rubber network is a combination of elastically effective and fluid-like components, as shown in Figure 5. However, there are some inconsistencies between the three models proposed by the groups of Toki, Tosaka and Ikeda mentioned above.⁵¹ In the models proposed by Toki's and Tosaka's

groups, SIC is assumed to occur in the domains with high crosslinking density, while the low crosslinking density domains are considered to be an incompressible fluid. However, the model proposed by Ikeda's group suggests that SIC occurs mostly in the rubbery matrix with low crosslinking density, while the high crosslinking density domains have a similar function to fillers.

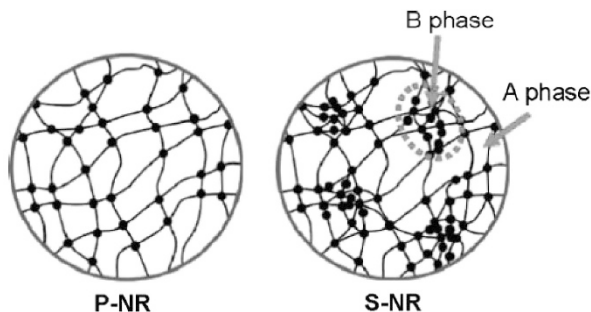


Figure 4 Speculated network morphologies of P-NR and S-NR. Reprinted with permission from Ikeda *et al.*³⁷ Copyright (2008) American Chemical Society. A full color version of this figure is available at *Polymer Journal* online.

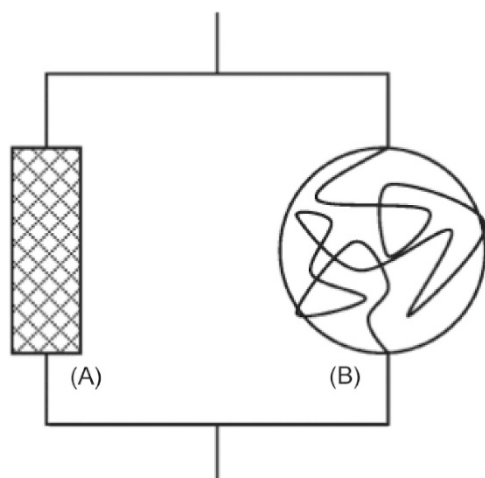


Figure 5 Mechanical model representing the coexistence of two types of network components. Component A is responsible for rubber elasticity, while component B is elastically ineffective, acting similar to a fluid mass. The former is illustrated as a rubber band, and the latter as a flexible bag filled with a viscoelastic liquid. Reprinted with permission from Tosaka *et al.*⁵⁰ Copyright (2009) American Chemical Society.

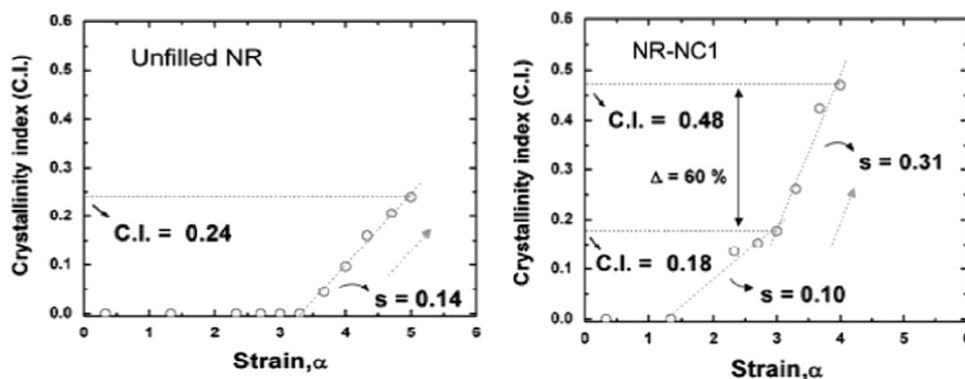


Figure 6 Crystallinity as a function of strain during stretching. Reprinted with permission from Carretero-González *et al.*⁶⁵ Copyright (2008) American Chemical Society. A full color version of this figure is available at *Polymer Journal* online.

Subsequently, Nie *et al.*⁵¹ proposed a three-phase model to explain the inhomogeneous network structure. They argued that the rubber network comprises three parts, that is, the high and low crosslinking density domains and a fluid-like component that has very low crosslinking density or no crosslinking points. They further assumed that SIC mainly occurs in the low crosslinking density domains, that the high crosslinking density domains act as reinforcing fillers and that the fluid-like phase does not contribute to SIC. Based on this three-phase model, they even established a visco-hyperelastic constitutive equation to calculate directly the quantitative distribution of the inhomogeneous network phases.⁵¹ They found that the inclusion of clay with a high specific surface area induces the uniformity of the network structure by decreasing the content of high crosslinking density domains and increasing the content of low crosslinking density domains.

The real condition is more complex than the above models. Namely, the domains with low crosslinking density may still have a chain-length distribution. However, directly probing how the chain-length polydispersity influences the SIC of polymers using experimental measurements is challenging. Thus, Zhang *et al.*³² performed dynamic Monte Carlo simulations to study the effects of chain-length distribution on the strain-induced crystal nucleation of polymer networks. A binary mixture of polymer networks with two different chain lengths was introduced. During the simulations, the long and short chains were stretched simultaneously. They found that a slight increase in the fraction of short chains could immediately lower the onset strains. Furthermore, both the short and long chains participate in early nucleation, but the crystallinity of the short chains begins to increase at slightly lower strains than that of the long chains. Based on these findings, they concluded that the two types of chains join together in crystal nucleation and growth but that the short-chain component, which has a higher degree of deformation at a certain strain, plays a more important role in determining the onset strain.

However, by combining the experimental observations based on WAXD measurements with a thermodynamic description, Candau *et al.*⁵² demonstrated that the presence of different crystallite populations is related to different network chain densities in stretched rubbers. During stretching, the crystallite population that is composed of the smallest crystallites forms first at the onset strain in the domains with the highest local crosslinking density. The larger crystallites form at a higher strain in the domains with a lower crosslinking density. Therefore, different network chains have different chain lengths and prefer to form crystallites of different sizes during stretching. Apparently, these findings are different to the simulation results

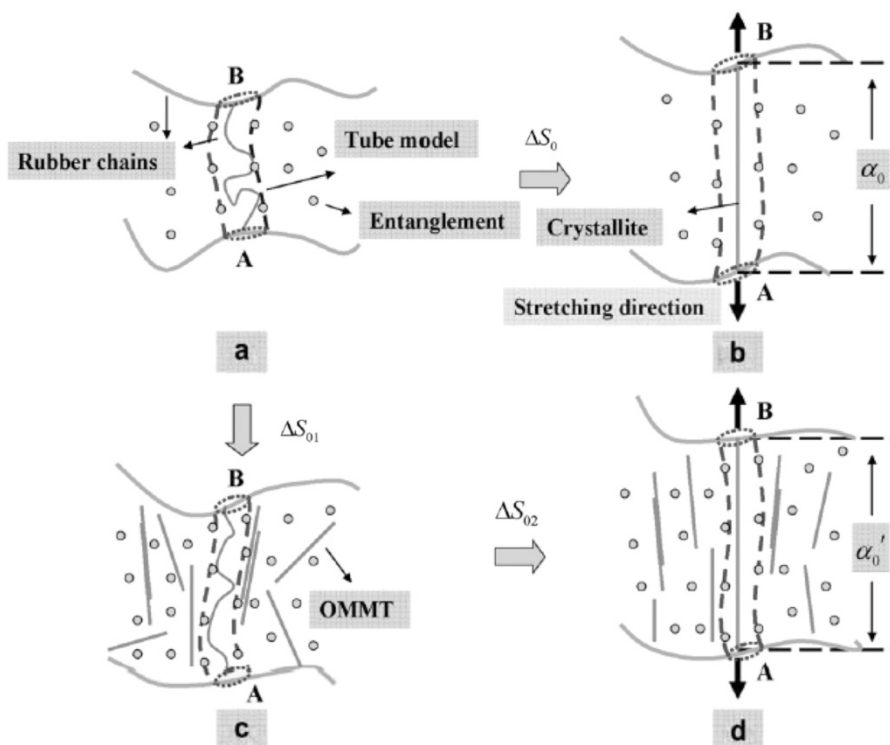


Figure 7 Schematic representation of structural evolution during stretching. Reprinted with permission from Nie *et al.*⁶⁷ Copyright (2011) Elsevier. A full color version of this figure is available at *Polymer Journal* online.

presented by Hu's group.³² This discrepancy may be derived from the different distributions of the network chains. In the simulation presented by Hu's group, the network chains with different chain lengths are mixed homogeneously, while Candau *et al.* proposed that the network chains of different lengths are distributed in different local regions. In short, the SIC behaviors of polymer networks containing nonuniform chain lengths are strongly dependent on the distribution of the network chains. If network chains of different lengths are mixed homogeneously, then the short and long chains will participate in nucleation together. Conversely, if the network chains of different lengths are distributed in different local regions, then strain-induced nucleation will first occur in the domains with the shortest network chains.

EFFECT OF NANOFILLERS ON SIC IN CROSSLINKED NR

Recently, it has been found that the inclusion of even a small amount of nanosized particles, such as nanoclays,^{13,53–55} carbon nanotubes^{56–58} or graphenes,^{59,60} can result in a remarkable enhancement of the mechanical properties of rubbers. However, the corresponding reinforcement mechanism is still poorly understood. For NR filled with conventional fillers (micron-sized fillers), the fillers behave as heterogeneities preventing the rubber chains from aligning and crystallizing, and thus the overall crystallinity is not increased compared with that of unfilled rubbers, although the presence of fillers may promote the crystal nucleation process.^{43,61–63} However, several studies have reported that the incorporation of nanoparticles leads to a dramatic improvement of SIC in NR.^{55,64–69} Carretero-González *et al.*^{64,65} investigated the effect of nanoclay on the structural evolution of NR during deformation. They found that adding highly anisotropic clay nanoparticles to NR induces an early onset as well as an enhancement of crystallization under deformation. A dual crystallization mechanism attributed to the alignment of clay layers during

stretching has also been observed, as shown in Figure 6.^{64,65} The neat rubber only shows a single crystallization step, while the rubber nanocomposites exhibit two crystallization steps: the first step at small strains related to the orientation of clay layers during deformation and the second corresponded to the conventional crystallization mechanism of unfilled NR. The dual crystallization process has also been observed in NR filled with other highly anisotropic nanofillers, such as carbon nanotubes.⁵⁶ Qu *et al.*⁶⁶ further demonstrated that an increase in the degree of exfoliation of the clay layers promotes the SIC of NR. In addition, using real-time mechano-optical behavior Liang *et al.*⁵⁴ detected that during stretching, the planar structures of the clay layers promote the parallel alignment of the rubber chains, and that the clay orientation increases as the clay content increases, which further promotes the SIC of rubber.

Using a combination of *in situ* synchrotron WAXD and the tube model,⁶⁷ Nie *et al.* analyzed the thermodynamics of SIC in P-NR filled with nanoclay. Interestingly, they stressed that the entropy change that was required for the onset of the SIC of the clay-filled rubber was composed of the entropy reductions due to constraints and stretching, as shown in Figure 7.⁶⁷ The presence of the clay layers would cause a reduction of the tube diameter (through enhancements of the topology entanglements and packing effects).^{70,71} In this case, the movement of the rubber chains will be restricted into a lower volume, and thus the conformational entropy will be reduced compared with the neat NR even before stretching. Furthermore, the onset strain for the clay-filled rubber will be much smaller than that for the neat rubber due to the entropy drop caused by the constraints before deformation. Another study further revealed that both the clay layers and the entanglements contribute to the constraints of the chains.⁷² In addition, the orientation of the clay layers during extension can accelerate a reduction of the conformational entropy, which controls the SIC process. At high strains, the clay layers align completely, and

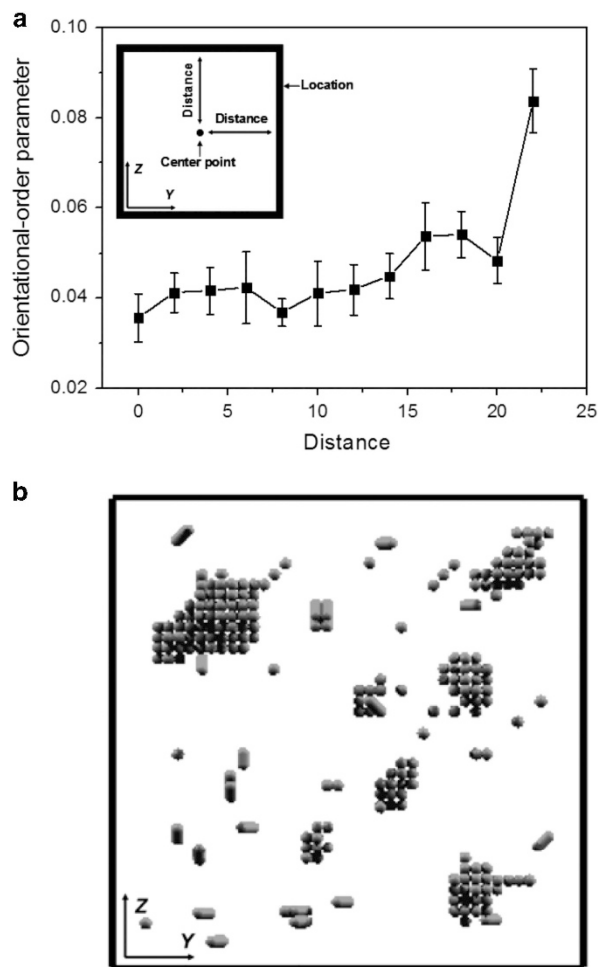


Figure 8 (a) Orientational order parameter of polymer bonds distributed in different locations at different distances from the center of the simulation box (before the onset of crystallization). The inset illustrates the definition of the locations. (b) Snapshot for strain-induced nuclei (red cylinders) at the onset strain of crystallization. The observation direction of this snapshot is along the stretching direction, and thus we could only see the circular end surface of the highly oriented nuclei. The black lines denote the polymer–filler interface. Reprinted with permission from Nie.⁷⁶ Copyright (2015) Springer. A full color version of this figure is available at *Polymer Journal* online.

their restriction of the rubber chain conformation becomes most severe. Thus, the rate of crystallization increases.

However, there are still some controversies regarding the clay-filled rubber. Generally, it is widely accepted that strong interactions exist between the rubber chains and organically modified clay^{13,53,55,64–66} due to the high specific surface area of the exfoliated layers. Saalwächter and colleagues^{73–75} systematically investigated the rubber–filler interactions and the network characteristics using NMR. Surprisingly, it was found that even exfoliated clay has obviously weaker interactions with the rubber matrix compared with conventional fillers, such as carbon black. Thus, they proposed that the significantly enhanced mechanical properties should be attributed to the filler network rather than to the rubber–filler interactions.⁷⁵ The formation of the filler network without strong polymer–filler interactions can also induce the improvement of the mechanical properties of NR. The filler network is also thought to influence the SIC process. However, only a few studies have focused on this issue. Through the use of dynamic Monte Carlo simulations, Nie⁷⁶ studied

the effect of the filler network confinement on the SIC of polymer networks. An enhancement of the confinement effect on the chains can be achieved by the reducing the lateral dimension of the simulation box. It was found that enhancing the confinement effect leads to a decrease in the onset strain. Therefore, the confinement effect of the filler network without polymer–filler attractive interactions is also beneficial for SIC. Furthermore, the confinement of the filler network to the chain segments leads to higher segmental orientation in the interfacial regions (as shown in Figure 8a). Those segments with higher orientation near the filler network join in crystal nucleation (Figure 8b), thus causing a reduction of the onset strain.

OTHER STRUCTURE FACTORS

Other factors that influence the SIC behaviors of NR include entanglements^{77,78} and non-rubber components.^{77,79,80} Numerous experiments have been carried out to investigate the contribution of entanglements to the mechanical properties of polymer materials.^{81,82} Thus, researchers believe that the presence of entanglements should also affect the SIC behaviors of NR. Zhao *et al.* investigated the SIC of NR with different strain rates at a fixed strain using synchrotron WAXD measurements. They found that at high strain rates, the entanglement points could act as crosslinking points.⁷⁸ However, at low strain rate the situation is more complex. According to the slip-link model,^{83,84} at low strains the trapped entanglements between the crosslinking points are able to slide and behave as slip-links.⁸⁵ At high strains those entanglements can no longer slip and behave as the crosslinking points.⁸⁵ Apparently, the slipping entanglements make no contribution to SIC at low strains, while the presence of the non-sliding entanglements promotes the SIC process at high strains. The role of entanglements is also controlled by temperature. Toki *et al.*⁷⁷ reported that the presence of entanglements in unvulcanized IR promotes the alignment of chains and induces crystallization during stretching at low temperatures but that entanglements cannot induce SIC at high temperatures. However, despite the recent advances in technology, probing the evolution of entanglements during stretching is still a challenge, and thus our understanding of the influence of entanglements on SIC is hindered. Molecular simulation that can be applied to identify entanglements^{86–89} should become a powerful tool for investigations aimed at elucidating the effect of entanglements on SIC in the future. Nevertheless, unlike unvulcanized IR, unvulcanized NR still shows SIC at high temperatures.⁷⁷ The different crystallization behaviors of unvulcanized NR and IR should be attributed to their structural differences: for example, NR has higher stereoregularity than IR. The simulation results of Hu's group demonstrated that the destruction of chain stereoregularity reduces the onset strain of crystallization.³⁰

SIC IN UNCROSSLINKED NR

Raw solid NR contains non-rubber components, including proteins, phospholipids, carbohydrates and metal ions.^{77,79,90} In addition, some functional groups exist at both ends of the rubber chains, which will link with the natural impurities to form a pseudoend-linked network.^{77,79,91,92} The appearance of the end-linked network in unvulcanized NR facilitates the occurrence of SIC.^{77,79} Toki *et al.* investigated the relationships between the network structure and SIC in unvulcanized NR. They found that the naturally occurring network in unvulcanized NR makes contributions to both SIC and stress–strain behaviors.⁷⁹ In addition, the end-linked network would also make the entanglements permanent where chains cannot loosen, thus promoting the SIC process.⁷⁷ However, to date, the roles of each non-rubber component and the functional groups have not been completely revealed.

The investigation of SIC of NR is helpful for researchers to understand the molecular mechanism of rubber reinforcements. For instance, it has been demonstrated that SIC with higher crystallinity occurs at the crack tip,^{93–97} where chains are overstrained compared with chains in the bulk, and thus the crack growth is hindered.^{98,99}

Although based on some advanced experimental measurements, such as synchrotron radiation micro-beam scanning X-ray diffraction⁹⁹ or infrared thermography and digital image correlation¹⁰⁰ more detailed information regarding the local structure or the heat source field in the crack tip zone has not been obtained, and we still do not have a complete understanding of the effects of SIC on crack growth.

CONCLUSION AND PROSPECTS

By using synchrotron WAXD some features of SIC have been identified. The fraction of the unoriented amorphous phase is still very high, even at high strains. Further investigations using molecular simulations revealed that the inhomogeneous distribution of the segment strains along a polymer chain rather than the distribution of crosslinking points is the main origin of the low fraction of oriented amorphous segments at high strains. In addition, a transition of the preferred nucleation mechanism from folded-chain nuclei to fringed-micelle nuclei with increasing strain was also observed.

There are several factors influencing the SIC behaviors of NR, such as network structures, nanofillers and some other structural factors in addition to the crosslinking points (entanglements, non-rubber components and pseudoend-linked networks). For instance, the onset strain of SIC of NR with a homogeneous network is dependent on the overall crosslinking density, while the onset strain with an inhomogeneous network depends on the local crosslinking density of elastically effective domains instead of the overall crosslinking density. The inclusion of nanofillers within the rubber matrix also changes the crystallization behavior. The crystallizability will be remarkably promoted due to the orientation of the nanofillers induced by stretching. As revealed by molecular simulations, in addition to the polymer–filler interactions, the confinement of filler networks also contributes to the improvement of crystallizability. Compared with synthetic rubber, NR contains some special structures, such as non-rubber components and pseudoend-linked network. Entanglements, non-rubber components and pseudoend-linked networks even exhibit a synergistic effect on the promotion of SIC.

In short, we believe that future investigations detailing the effects of network structures, nanofillers, entanglements and non-rubber components on SIC will be research hotspots in the field of polymer science. In order to obtain direct correlations between SIC and microscopic structures, rubbers with controlled structures should be synthesized first. Furthermore, researchers should investigate the structural characteristics to further the understanding of the effects of non-rubber components on SIC. Moreover, molecular simulations, which can observe molecular structures or motions directly, could be an effective supplement for experiments. For instance, although directly observing entanglements in experiments is a challenge, entanglements can be directly detected by molecular simulations. Thus, we believe that in the future the molecular mechanisms of SIC and rubber reinforcement will be completely uncovered through a combination of experiments and simulations.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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