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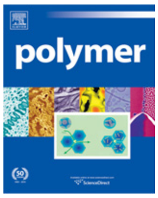

“Mechanism of the self-reinforcement of cross-linked NR generated through the strain-induced crystallization”

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ABSTRACT

The author proposed new models and concept for the self-reinforcement of NR. The first model indicates that general rubber vulcanizate consists of the heterogeneous structure, partially continuous cross-linked phase (75%) and continuous uncross-linked phase (25%). In addition, the author proposed other new models and concept for the strain-induced crystallization in vulcanized NR, in which the strain-induced crystallization takes place in the uncross-linked phase in cross-linked rubber. In the uncross-linked phase under large extension, molecular flow and orientation occur due to the very high compressive, shear and tensile stresses generated by the surrounding hard cross-linked phases, which makes the strain-induced crystallization possible in the uncross-linked phase. As macroscopic extension increases, the crystallization spreads over the whole uncross-linked phases, thus the uncross-linked phase changes its character from original soft rubber to the strong super network consisting of a bundle of extended molecules interconnected at the crystals. The characteristic phenomena observed in the stress–strain relation of NR such as the stress-upturn, high tensile strength and large stress-softening (Mullins effect) can be reasonably explained using these models and concepts.

1. Introduction

Natural rubber (NR, cis-1,4-polyisoprene) vulcanizates show great physical and mechanical properties in tensile strength and fatigue resistance, together with high hysteresis energy. Since these characteristics take place without addition of any filler, we call them the self-reinforcement of NR. In particular, its high tensile strength (20–30 MPa) and large strain at break (800–1000%) are excellent in comparison with the case of unfilled SBR (Styrene Butadiene Rubber) vulcanizate where the tensile strength is about 1.5–2 MPa and the strain at break is 400–500%.

On the other hand, it is widely recognized that the high tensile strength of NR decreases with increasing temperature [1,2]. In particular, it drops abruptly to almost the same level (2–3 MPa) as that of SBR at a higher temperature than 100 °C. The critical temperature agrees well with another critical temperature where no strain-induced crystallization occurs. Furthermore, we know that the abrupt drop of tensile strength in NR takes place when the flaw size included in specimen is bigger than the critical size [2,3]. This phenomenon is so understood that when a specimen includes big flaws, fracture propagates very fast, and as a result, there is no time for the strain-induced crystallization to occur in the specimen. These phenomena indicate that when the strain-induced crystallization does not occur, there is no fundamental difference between NR and SBR.

Another characteristic in NR vulcanizates is that the tensile strength is only slightly reinforced by filling with carbon black. This is in great contrast with the case of SBR. In unfilled SBR, although its tensile strength is 1.5–2 MPa, it increases to 30 MPa by filling with carbon black. It may indicate that the mechanism of the self-reinforcement of NR may be similar to the mechanism that SBR is reinforced by filling with carbon black. In reality, there are many similarities between the unfilled NR and the carbon black-filled SBR, not only in the tensile strength, but in the great stress increase under large extension (called the stress-upturn) and large hysteresis energy (the Mullins effect).

Although numerous ideas, models and theories have been proposed to explain the strain-induced crystallization and the self-reinforcement of cross-linked NR, the following fundamental questions have been left unanswered;

(1) How do cross-linked molecules crystallize in vulcanized rubber? Most proposals for the strain-induced crystallization in NR given so far recognize a priori that the crystallization takes place within the cross-linked molecular structure, while

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the experimental and theoretical conclusions in the polymer science of crystallization clearly indicate that for the crystallization of polymer molecules they must diffuse freely in the system and of course cross-links block crystallization extremely.

(2) Why does the system containing strain-induced crystals generate the large stress increase (the stress-upturn) at large extension? According to the Guth equation [4], the filling of crystals of 20% volume fraction only increases the stress of the unfilled rubber by two over all strain amplitudes.

(3) Why is the structure that includes the strain-induced crystals able to sustain the great stress of the system under large extension? In other words, what structure does yield the great tensile strength of NR (25 MPa)? In the system that crystals play only a role of dispersed fillers, obviously it is the matrix cross-linked rubber that supports such a great stress of the system, whereas the strength of the matrix rubber itself (without crystals) is 2–3 MPa at most.

(4) Why does the stress decrease abruptly when the unloading process begins (Mullins effect)?

(5) Why is vulcanized NR scarcely reinforced by filling with carbon black, whereas SBR is greatly reinforced by the filler?

The author discussed and proposed new models and concepts for the reinforcement of carbon black-filled rubber [5] and polyurethane [6] where is concluded that for the great reinforcement of elastomers, it is indispensably necessary for the continuous hard and strong phase to be newly constructed in the system instead of the weak matrix rubber. On the same concept, the author [6–8] has proposed a few models and ideas for the self-reinforcement of NR vulcanizates from the viewpoints of the mechanism of self-reinforcement based on FEM stress analysis, which is quite similar to those for the carbon black reinforcement of rubbers.

The purpose of this report is, first to propose a general structural model for cross-linked rubbers and second connect it to the strain-induced crystallization in the cross-linked NR and in addition make the mechanism of the self-reinforcement of NR clear, and finally give the answer to the above numerous questions.

2. Historical background

Treloar [9] performed the famous calculation to explain the stress-upturn observed in NR using the non-Gaussian treatment given by Kuhn and Grün [10], where the stress-upturn occurs without the influence of strain-induced crystallization. When the molecular motion is constrained within the limited molecular length between cross-links, the strong stress-upturn in the stress–strain curve under large extension is the direct consequence of the finite extensibility of molecular chain between cross-links. The stress-upturn of NR, however, is closely related to the strain-induced crystallization under large extension, and when the crystallization does not occur the vulcanized NR behaves like SBR, and just like the Gaussian chain. Thus, the new question is why the stress-upturn does not occur in the real vulcanized rubber (including SBR and NR) under the un-crystallizable condition.

The "ideal network" used for the theoretical consideration of the cross-linked material is based on the assumption that the network has a homogeneous structure, with a very narrow molecular weight distribution between cross-links and a unique functionality of cross-linking but no occupied volume. However, the polymerization methods generally used to produce polymer networks cannot be controlled for network formation, because radical co-polymerization is basically a random process. Recent simulations [11,12] for gelation obviously show the existence of microscopic and macroscopic heterogeneities in the cross-linked networks consisting of cross-linked and uncross-linked structures.

Folland and Charlesby [13] measured the spin–spin relaxation times T_2 of cross-linked IR using the pulsed NMR method and found that the cross-linked IR consists of two regions, the heavily cross-linked component (82%) and the uncross-linked one (18%). The same measurements [13–17] have been performed for various rubber vulcanizates which gave almost the similar values. However since the T_{2S} component measured by the pulsed NMR includes not only chemical cross-links but physical molecular entanglement, the heavily cross-linked component may be smaller than the above values. Thus the uncross-linked component must be 20–30% in volume fraction.

The recent conclusion in the theory of the crystallization of polymers, whether from dilute solution or melted state, is so understood that the process in which a long molecular chain is extended and folded and becomes lamella structure, strongly depends on diffusion of entangled molecules. That is, it is essential for the formation of lamella that a molecule must diffuse freely to nuclei sliding along the nucleus axis, after being unfastened from molecular entanglements. In other case, when polymers are strongly compressed or sheared between plates i.e. by extrusion or stirred rotationally, molecules orientate and extend to the extension direction, and finally make extended nuclei (shish). Other molecules gather together and conglutinate around the nuclei and grow as lamella (kebab).

Crystalline structures in un-vulcanized NR were first observed by Andrews [18,19] with TEM techniques. Recently, several studies [20–22] have showed that the shish–kebab structure is lamellae and it grows laterally to the a-axis direction. It means that when the un-vulcanized NR is stretched at room temperature, first thin nuclei (shish) are formed parallel to the extension direction, following which lamellae (kebab) grows laterally to the nuclei, perpendicular to the extension direction. All of the data [18–22] shows the thickness of the lamella to be 5–15 nm.

Yau and Stein [23] evaluated the strain-induced crystallization of vulcanized NR at room temperature using the low-angle light scattering technique and concluded that the structures detected in the vulcanized NR is the same as observed in the un-vulcanized NR by Andrews. Recent results indicate that the lateral crystal size in the vulcanized NR is 10–15 nm [24–26]. Thus, we will be able to say that the strain-induced crystals in the vulcanized NR basically consist~~s~~ of the same structures in the un-vulcanized NR, i.e. lamella structures (shish) with thin nuclei (kebab).

Toki and co-workers [27–29] measured the molecular orientation and the strain-induced crystallization of vulcanized NR under extension in detail using the in-situ synchrotron WAXD. They evaluated amorphous halos and concluded that even at the highest strain, most chains remained un-orientated and only a minor portion of molecules in the system orientated during extension. This is important to understand the mechanism of self-reinforcement of NR, because we have had an image that before crystallization, most of the molecular chains orientate first and some parts of the orientated molecules begin to crystallize successively. These results show that in vulcanized NR, only a limited portion of molecules orientates and crystallizes and other major portions can neither orientate nor crystallize, remaining un-deformed even at the highest strain.

Trabelsi et al. [24] measured the strain-induced crystallization of carbon black-filled and unfilled NR at room temperature. In the filled NR, both the stress-upturn and the strain-induced crystallization occurred at about 100% strain, a much smaller strain than for the case~~s~~ of unfilled NR. However, the final crystallinity at a large extension for the filled NR seems to be almost equal to that for the unfilled NR. This similarity indicates that the filling of carbon black only makes the strain-induced crystallization in the filled NR much faster compared with the case of the unfilled NR.

The recent data indicates that the total fraction to be able to orient and crystallize in the vulcanized NR under large extension is 20–25% in the system [24,27–30]. However, under consideration of the limitation that the crystallinity of polymer is 80–90%, the total volume fraction for orientation and crystallization must be slightly higher than these values, i.e. 25–30% in the system.

Concerning the influence of cross-links on the crystallization of NR, Andrews [19] suggested that cross-links suppressed crystallization, in particular for the nucleation stage. Gent [31], Yau and Stein [32] and Mandelkern [33] also pointed out that cross-links interfered with the crystallization process in the proximity of cross-links, thus increasing structural irregularities and causing chain mobility to be reduced, resulting in the reduction of the crystalline dimensions.

Göritz and Kiss [34] investigated the entropy reduction of the stretched sample of cross-linked Polybutadiene rubber. After being stretched to $\lambda = 4$ at room temperature (295 K), the sample was cooled down to 261 K. Two melting points were observed separately in the above specimen. One corresponds to the crystals grown at 261 K and the other to that produced by the strain-induced crystallization at room temperature, the latter being 50 K higher than the former. They reached the important conclusion that the strain-induced crystallization must occur in a limited circumstance where molecules are extremely highly orientated compared with other matrix regions. It means that under large extensions, two regions appear, i.e. very highly extended and slightly extended, and the strain-induced crystallization occurs only in the very highly orientated region.

This is a very important conclusion in relation with the results measured with WAXD. Both the results surely indicate that there are two regions in the largely stretched NR, that is, one is the minor region in which molecules are very highly extended and the strain-induced crystallization takes place and another is the major region in which molecules are slightly extended and probably the crystallization does not occur.

3. Experiments

3.1. Mechanical testing

The high tensile strength of NR abruptly drops to almost the same level as that of SBR (2 MPa) at a temperature higher than 100 °C. In this experiment, however, there is an uncertainty that the higher temperature causes degradation of rubber networks, which result in the much lower tensile strength. Therefore, preceding the main discussion, the following point is clarified: Ring shape specimens were prepared and their stress–strain relations were measured at 25 °C, 90 °C and 100 °C. In addition, other specimens were prepared for the measurement at 25 °C, which had previously undergone the same temperature conditioning as the samples measured at 100 °C, i.e. being kept for 60 min at 100 °C. Both results measured at 25 °C were compared together. The compounding recipe (phr, parts per hundred rubber) of unfilled NR used in this paper is, ZnO = 5, Stearic acid = 2, vulcanization accelerator = 0.5, antioxidant = 0.5, and sulfur content being changed. HAF carbon black (50 phr) was added to NR and SBR vulcanizates.

3.2. Model experiment to estimate the molecular orientation

To understand the influence of irregularities on the orientation of regular networks under large extensions, we did the model experiment using a plane string net (for gardening) consisting of square lattices. Two types of specimen, a regular lattice and an irregular lattice were prepared. In the specimen with the irregular lattice three additional strings were given to the regular lattice, as irregular knots. Both specimens were extended uniaxially on a plate. This is very important to understand the difficulties of the orientation and crystallization of molecules in the cross-linked NR.

4. Results

4.1. Stress–strain behaviour of NR vulcanizates

Fig. 1 shows stress–strain curves of vulcanized rubbers of various types. The unfilled NR shows the typical stress–strain curve at room temperature, the clear stress-upturn and a high tensile strength of 25 MPa. However at 90 °C, it does not give the stress-upturn, similar to the case of SBR measured at room temperature. Both curves can roughly be represented by the Gaussian chains, giving an image that the distance between cross-links is infinity, just like un-vulcanized rubbers. Fig. 2 shows more detailed information about the stress–strain curves of vulcanized NR of various sulfur contents measured at 100 °C, where the stress-upturn is not observed, the tensile strength being 2–4 MPa. This result indicates that the real vulcanized rubber behaves as the Gaussian chain when it does not include the strain-induced crystals.

Fig. 1 also shows the similarity of stress–strain curves between unfilled NR and filled NR and between filled NR and filled SBR. The stress–strain curve of the filled NR can be regarded as the shifted one from the unfilled NR by a strain of 300–350%. It seems to suggest that the self-reinforcement in NR will be generated by the same mechanism as that in the reinforcement of the carbon black-filled SBR and NR. As discussed elsewhere [5], the essential point in the carbon black-reinforced SBR is that the continuously connected uncross-linked molecules (bound rubber) surrounding carbon particles extend and orientate under large extensions, and finally construct the super network consisting of bundles of extended molecules interconnected at the carbon particles. This super network supports the very high stress of the system under large extension and thus gives the stress-upturn and the great tensile strength of 30 MPa. In view of the similarity of the stress–strain curves, we can suppose that the same mechanism must work on the self-reinforcement of NR, discussed later.

Fig. 3 shows the tensile strength of unfilled NR measured at 24 °C (open circle) and 100 °C (open triangle). Fig. 3 also includes other data measured at 24 °C (filled circle), which was previously held for 60 min at 100 °C. There is a good agreement of the tensile

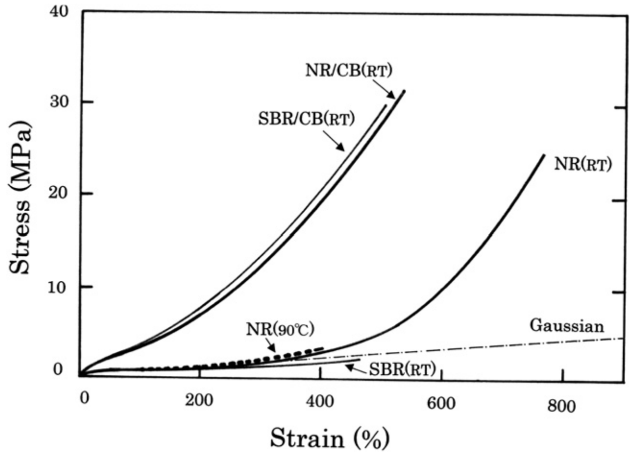

Fig. 1. Stress–Strain relations of filled and unfilled rubber vulcanizates (NR and SBR) measured at room temperature and 90 °C.

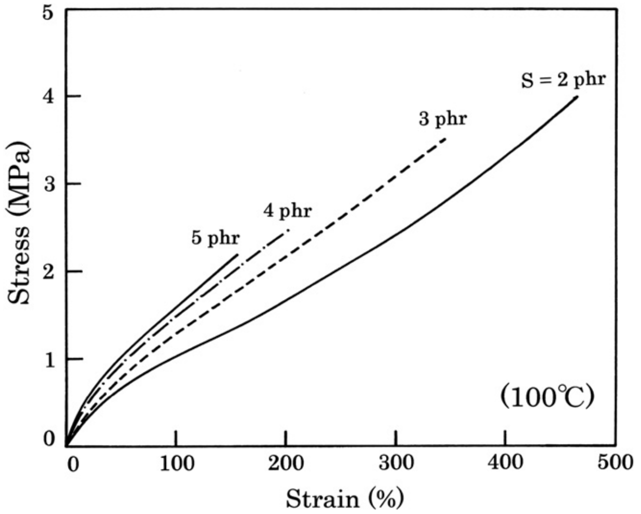

Fig. 2. Stress–strain curves of vulcanized NR for various sulfur contents measured at 100 °C.

strengths between both samples (open and filled circles) measured at 24 °C, which indicates that there is no chemical degradation in NR during a short time measurement at 100 °C.

Fig. 4 shows stress–strain curves of unfilled NR of various sulfur contents at room temperature. Although the stress of un-vulcanized rubber ($S = 0$) does not increase under large extension, the stress of the vulcanized rubbers becomes larger and larger as extension increases. Thus, the stress difference between the un-vulcanized and vulcanized rubbers becomes larger as extension increases. Under a very large extension of more than 300% in which the strain-induced crystallization begins to occur, the stress difference between the un-vulcanized and vulcanized rubbers will be larger than 50–100 times, for example. This is quite important when we consider the modulus difference between the cross-linked and uncross-linked phases in the heterogeneous structure of the real vulcanized NR, discussed in detail later.

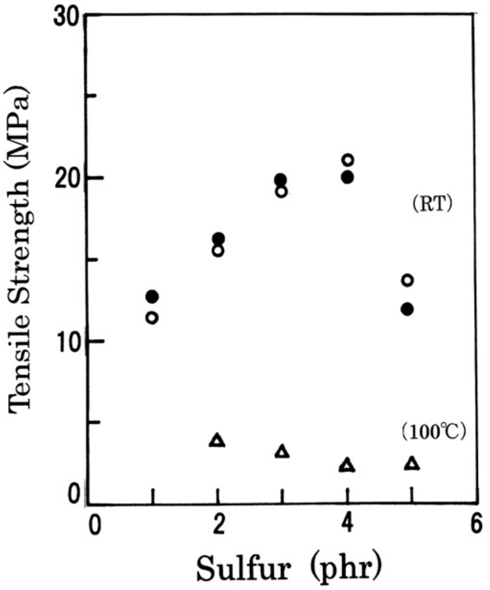

Fig. 3. Tensile strength of NR measured at 24 °C(○; virgin, ●; undergone at 100 °C) and at 100 °C(□), using a ring shape specimen.

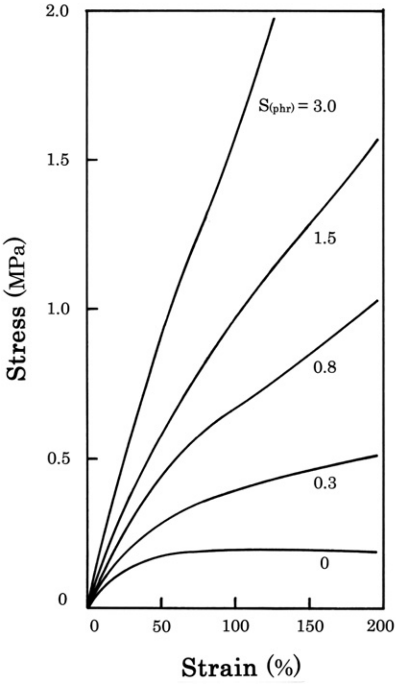

Fig. 4. Stress–strain relations of NR as a function of sulfur content measured at room temperature.

4.2. Molecular orientation in the cross-linked system

Fig. 5 shows the plane string nets of regular lattice (Fig. 5A) and irregular lattice (Fig. 5B). In the net of irregular lattice, three additional strings of the same length (a, b, c) are securely tied to the regular knots. When the specimens are extended (indicated by an arrow), the net of regular lattice deforms homogeneously and produces the regularly-orientated lattice, as shown in Fig. 6A. On the other hand, in the net of irregular lattice, only three additional interconnected strings disturb the regular orientation of the net severely, whose irregularity is spread over the area surrounding three interconnected points, as shown by the ellipse of the broken line in Fig. 6B.

Generally, for the modeling or theoretical calculation of the stress–strain relation of the cross-linked molecules, the perfect regular network is adopted a priori, i.e. for the cross-link density, the molecular length between cross-links and the number of molecules consisting of a cross-link junction, for example. However, in the real cross-linked rubber, as is well known, there exist many kinds of irregularity due to the very wide distribution of the above characters in addition to their occupied volume in these cross-link junctions. Therefore, we can surely say that in such real cross-linked rubbers, the idealized homogeneous and regular extension and orientation of all molecules simultaneously in the system before crystallization must be quite difficult. This is one of the key factors for understanding the morphological structures of the real vulcanized rubbers.

5. Discussion

5.1. Proposal of new models for the heterogeneous structures in cross-linked rubber

In the initial Historical Background, we could conclude that cross-linked rubber has the heterogeneous structures consisting of the densely cross-linked phase and the rare cross-linked or

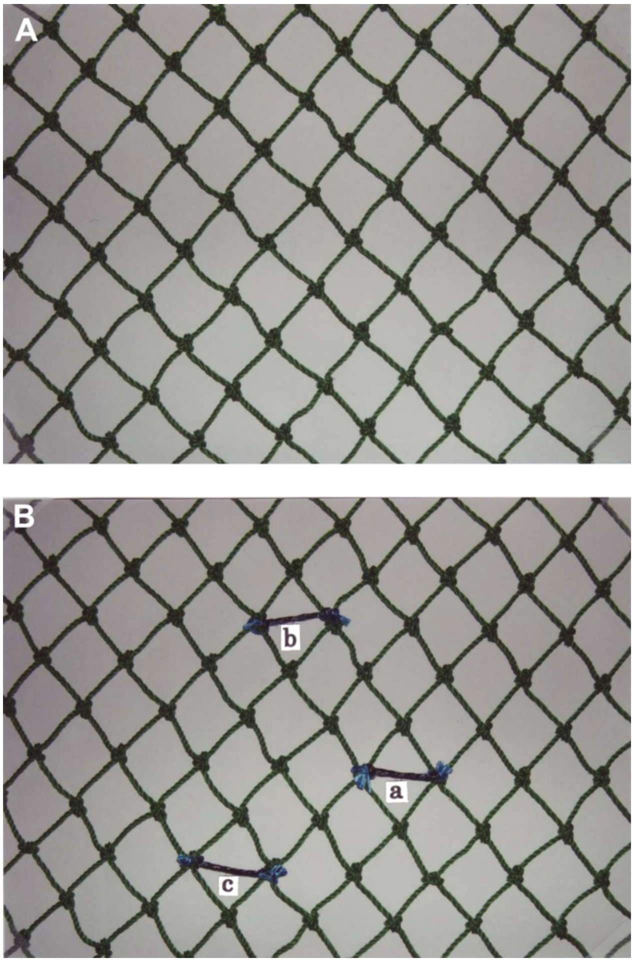

Fig. 5. Plane string nets of regular lattice (A) and irregular lattice indicated by a, b, c (B).

uncross-linked phase. Very recently, in addition, several important reports have been published directly to show the heterogeneous cross-linked structures in vulcanized rubbers. Dohi and Horiuchi [35,36] observed the heterogeneous dispersion of sulfur in the vulcanized SBR using two kinds of electron microscopic techniques and showed that sulfur is mainly adsorbed on the surface of ZnO (50–100 nm) and only partially dispersed in matrix rubber. They showed photographs indicating that in the matrix rubber, sulfur is distributed not homogeneously but quite heterogeneously as the aggregates of ZnS. Thus, it was made clear that the cross-links produced by the sulfur reaction does give not an idealized homogeneous networks (linked by each sulfur atom) at all, but many kinds of heterogeneous structures composed of ZnO of 100 nm, the huge aggregates of ZnS of a few tens −50 nm and other small amount of dispersed sulfur atoms.

Nukaga and Watabe et al. [37,38] observed the heterogeneous cross-link structure in vulcanized NR using atomic force microscopy (AFM) and showed that in the vulcanized NR two components of different modulus, soft phase (5.4 MPa) and hard phase (137 MPa). Under extension the soft phase extends mainly and the hard phase scarcely does. They suggested that the heterogeneous cross-linked structures might include two domains of different size, several tens of nm and a μm scales. Furthermore, Iwabuki et al. [39] measured the mobility of the heavily cross-linked and uncross-linked phases under extension using the pulsed NMR method. With increasing strain amplitude, the mobility of the uncross-linked phase decreased conspicuously until coming to the crystallization, whereas the heavily cross-linked phase decreased slightly under large extension. They considered that the soft uncross-linked phases extended and oriented mainly under large extension and changed their character to the hard crystals.

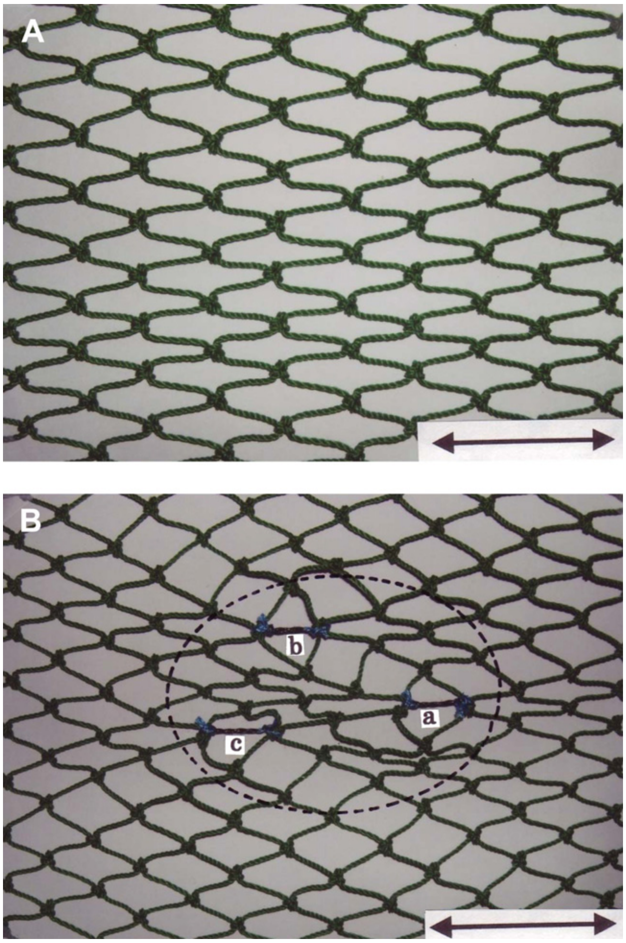

Fig. 6. As Fig. 5, but under extension: regularly-oriented lattice (A) and irregularly-oriented lattice spreading over the ellipse of broken line (B).

The above newly presented information and the previous historical backgrounds, undoubtedly permit us come to the conclusion that the cross-linked rubber consists of two phases of different cross-link density, the densely cross-linked phase and the uncross-linked phase. In addition, due to the experimental results [13–17,24,27–30], we can roughly estimate that their volume fraction in the cross-linked rubber must be 25 (±5)% for the uncross-linked phase and 75 (±5)% for the densely cross-linked phase. Under extension, the uncross-linked phase extends the most and preferentially, and this results in the heterogeneous deformation, i.e. the non-affine deformation.

Now, the author would like to propose a new structure model for real cross-linked rubber from the total consideration given so far. The new model is based on the following assumption.

○ The vulcanized rubber consists of the uncross-linked (25%) and cross-linked phases(75%).

● The uncross-linked phase is continuous and the cross-linked phase is partially continuous. Concerning the second assumption, although the cross-linked phase may fundamentally be discontinuous, the cross-linked phase of 75% corresponds to the occupation of the closest packing and thus, some continuity must exist at the boundaries connecting the cross-linked phases. The second assumption is also supported by the fact that the modulus of the vulcanized rubber increases with sulfur content, which indicates the effect of cross-links on the modulus of the system as shown in Fig. 4. On the contrary, if the uncross-linked phase is discontinuous and dispersed in the cross-linked phase, it is quite difficult for the minor uncross-linked phase (surrounded by the hard cross-linked phases) to deform the most and preferentially under extension and swelling. The morphology of such a system that the minor component (25%) is continuous and the major component (75%) is partially continuous seems to be similar to the structure of the physical gel produced by polymer (15% in volume fraction) and oil (85%) presented by Fukahori and Mashita [40]. The morphological structure of the gel shows that the major component (oil) is enclosed within the continuously interconnected spherical shells of the minor component (polymer) and in addition, several small holes were bored through the interconnected surfaces of the shells. Thus, the oil phase enclosed in the polymer shell is also connected continuously to each other by the holes.

▲ The boundary between the uncross-linked and cross-linked phases is strongly connected with each other by chemical cross-links or tight entanglement of molecules, because it is found that the uncross-linked phase is not extracted from the vulcanized rubber with good solvent.

Now, the author proposes a new model of heterogeneously cross-linked structure generally acceptable for most cross-linked rubbers, which is a two-phase model simplified for the real complicated cross-link structures, as shown in Fig. 7. In Fig. 7 (two dimensional), the cross-linked phase (square networks) partially connected with each other is surrounded by the continuous uncross-linked phase (vacant). The more detailed expression is given in Fig. 8, in which square networks represent the cross-linked phase and surrounding hand-writing loops show the uncross-linked phase. The structures given by Fig. 8 transforms into those in Fig. 9 under extension, where the macroscopic extension direction is vertical. In these models, the interface between cross-linked and uncross-linked phases is connected to each other by chemical cross-links or tight molecular entanglements. In Figs. 8 and 9, L_X and L_Y are typical spots to be compressed horizontally

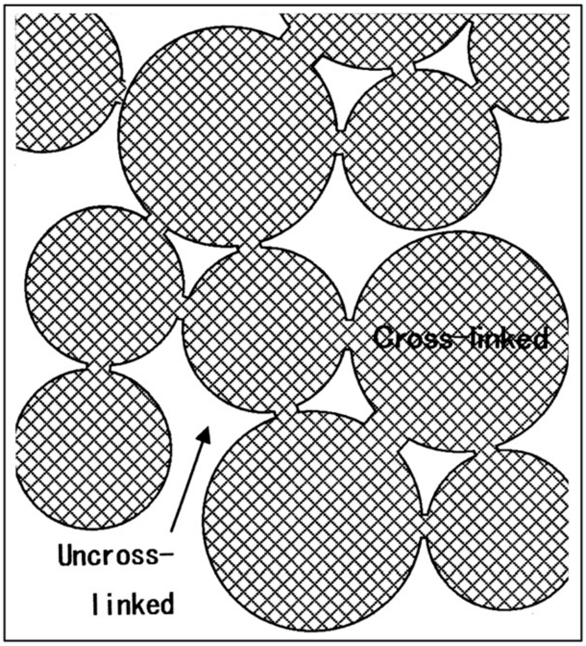

Fig. 7. New model to reveal the inhomogeneous structures in general vulcanized rubbers (two dimensional).

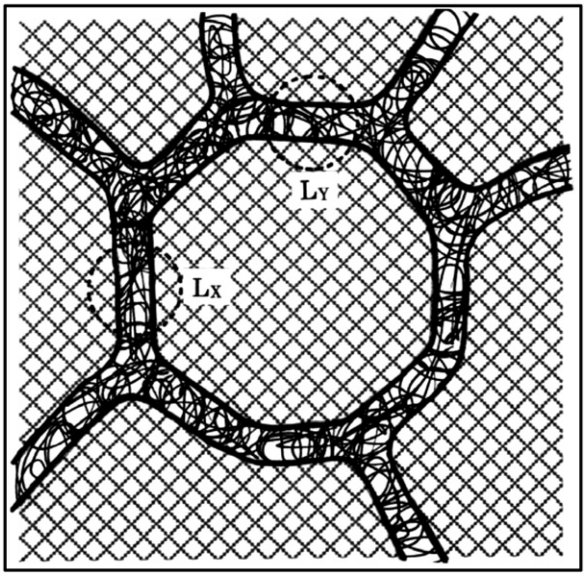

Fig. 8. Detailed expression of Fig. 7.

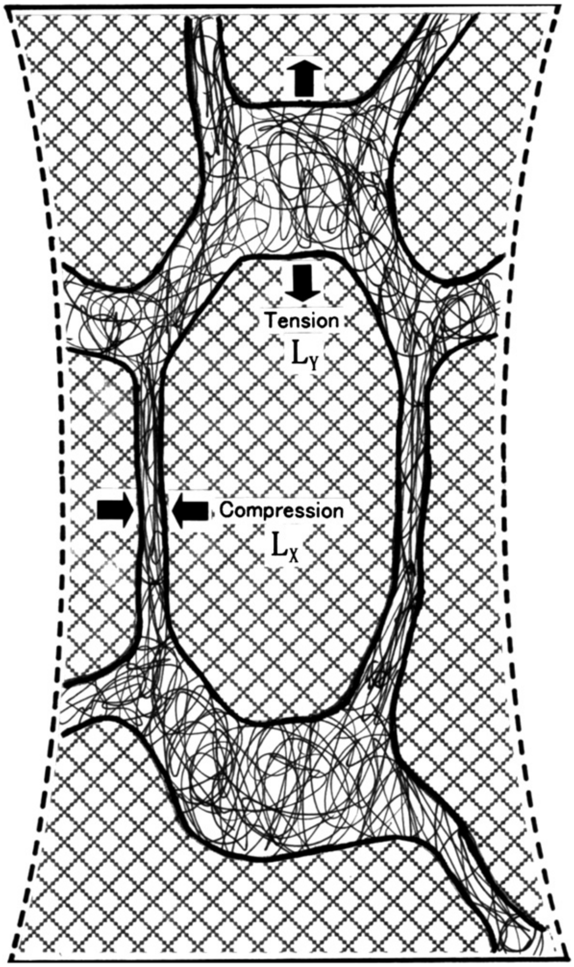

Fig. 9. Deformed state of Fig. 8.

and extended vertically under macroscopic vertical extension, respectively.

In Fig. 9, when the system is macroscopically extended uniaxially, the soft uncross-linked L_Y spot sandwiched between hard cross-linked phases is preferentially extended to the extension direction. This seems to be the reason why the cross-linked rubbers such as SBR at room temperature and NR at 100 °C behave like Gaussian chains (no cross-links), because the main parts to deform under extension are these uncross-linked phases and as a result, the modulus of the system becomes very low. At the present stage, we assume the fundamental size of the cross-linked phase given in Figs. 7 and 8 to be 100–1000 nm. Under very large extension, these structures may orientate to the extension direction and make much larger scale features (1–10 μm) [37,38]. Thus, the continuous uncross-linked phase basically becomes the origin of fracture under large extension, which results in the very low tensile strength in SBR and NR at high temperature.

5.2. *The paradox problems in the strain-induced crystallization of cross-linked rubber*

Preceding the proposal of a new model, now we summarize the information concerning the strain-induced crystallization of the cross-linked rubber, based on the initial Historical Background and the very recent information given previously [35–39].

- ○ The self-reinforcement based on the stress-upturn in NR is a continuous process from the strain-induced crystallization to the finite extension of the molecules. It is also true that in reality, the strain-induced crystallization occurs in the cross-linked NR under large extension. The crystals thus produced through the strain-induced crystallization in the cross-linked NR are mainly composed of lamella structures with the shish–kebab bone.
- ● However on the other hand, in the formation of lamella and shish–kebab structures, it is essential that molecules diffuse and slide freely to nuclei released from entanglements. In this situation, cross-links are not only expelled from the crystals as defects, but absolutely obstruct the free diffusion of molecules, and thus prevent the crystallization of polymers severely. As presented in the model experiment with a plane string (Fig. 6), cross-links also inhibit the regular orientation of molecules. Of course, we know that cross-links have a very large distribution in length and functionality and a very big excluded volume, and as a result they must prevent the orientation and the finite extension of molecules. Thus, the fact that the strain-induced crystallization takes place in the real cross-linked NR gives us a quite serious paradox problem.
- ▲ Meanwhile, we know that the vulcanized rubber consists of two phases of different cross-link density, the densely cross-linked phase (75%) and the uncross-linked phase (25%), in which the uncross-linked phase and the cross-linked phase are continuous and partially continuous, respectively. Therefore, it seems to be that the only way to solve this paradox problem is to consider that the strain-induced crystallization takes place within the uncross-linked phase (not in the cross-linked phase) in cross-linked rubber. In the conventional understanding, the cross-linked rubber and the cross-linked phase were considered to be the same matter, thus people could not help but misunderstand that the strain-induced crystallization occurs in the cross-linked phase. Most importantly, we must distinguish the cross-linked phase in the cross-linked rubber and the cross-linked rubber itself very clearly to solve the above paradox.

5.3. *Proposal of a new model for the strain-induced crystallization in NR*

Now, the author proposes a new model for the strain-induced crystallization of NR, as shown in Fig. 10. The strain-induced crystallization takes place in the uncross-linked phase given in Fig. 10, released from the absolute constraint by cross-links. In this model, however, the fundamental questions will be why and how the crystallization occurs in such a narrow uncross-linked phase sandwiched between cross-linked phases. In other words, what is the direct driving force to generate the strain-induced crystallization in the uncross-linked phase? This is an important question, because in usual un-vulcanized NR, the strain-induced crystallization and the following stress-upturn are not generated under general tensile testing at room temperature, as shown in Fig. 4 ($S = 0$).

Fig. 11 is the FEM stress analysis modified from the result given by the Fukahori and Seki [41] to show the contour map of the stress concentration factor α ($= \sigma/\sigma_0$, σ the maximum principle stress and σ_0 the uniform (average) stress) generated around rigid spheres, when the volume fraction of the sphere is 20% and an average strain is 10%. In Fig. 11, the dotted lines ($\alpha \geqq 1$) correspond to tensile stress and the solid lines ($\alpha < 1$) to compressive stress, with an arrow indicating the macroscopic extension direction. Therefore, if the volume fraction of the rigid particles is 75%, there must be generated the extremely strong tensile and compressive stress around the hard particle. As discussed in Fig. 4, the modulus of vulcanized NR is about 50–100 times larger than that of un-vulcanized NR at

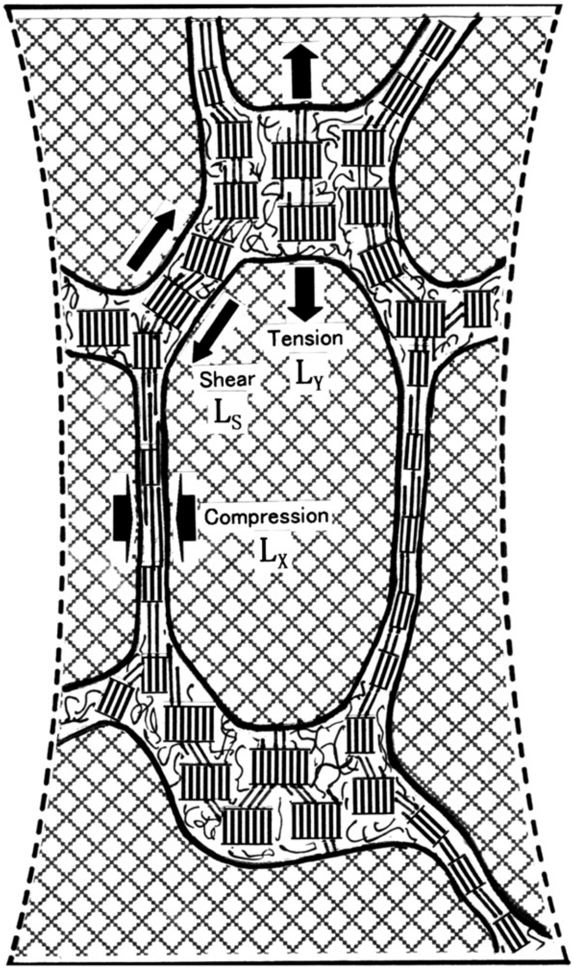

Fig. 10. Super network produced through the strain-induced crystallization in the vulcanized NR.

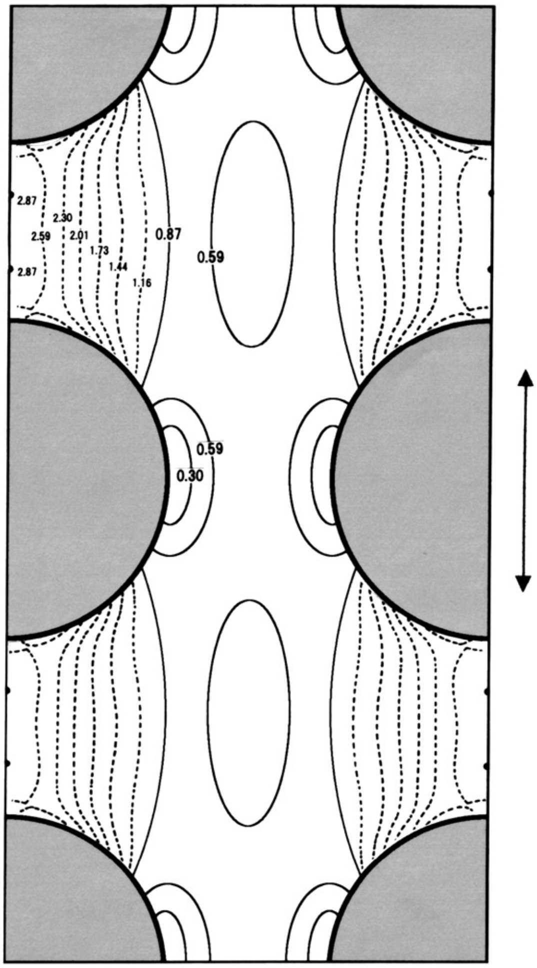

Fig. 11. Contour map of the stress concentration factor in the hard sphere-filled system ($\phi = 0.2$).

a strain of 300%. Furthermore, in the vulcanized rubber the cross-linked phase is surrounded by the continuous uncross-linked phase and only a minor portion is connected with each other as the continuous phase as shown in Fig. 7, then the modulus of the truly cross-linked phase must be much higher than that of the uncross-linked phase. Thus, we consider that the cross-linked phases work as the hard phases in the cross-linked rubber. Therefore, the soft uncross-linked phase in the L_Y part in Figs. 7–9 is extended extremely by tensile force generated between the hard cross-linked phases. In the L_X and L_S parts, of course, the very high compressive and shear forces work, which is similar to the process of extrusion or rotational stirring. Thus, the orientated and finitely extended molecules seem to nucleate as shish and other molecules conglutinate around the nuclei and grow as lamella (kebab). These situations are represented in Fig. 10, which seems to be applicable to most crystallizable rubbers such as NR, IR and BR. Since the hard cross-linked phase is extended greatly only at a minor connected part (Fig. 7), the major block region of the cross-linked phase deforms its external shape only slightly to the extension direction even under large extension. Such behaviour is observed in swollen gels and vulcanized rubbers [42].

5.4. Mechanism of the stress-upturn originated from the strain-induced crystallization

Now we consider the mechanism of the stress-upturn in NR. It is undoubtedly true that the stress-upturn is the consequence of the finite extension of molecules under large extension as verified by Treloar [9]. However as is well understood, the strain-induced crystallization itself lowers the stress of the system due to the entropy reduction of extended molecules, which has been shown experimentally [27,43,44].

The crystals (20% in volume fraction) produced through the strain-induced crystallization first play a role to fix uncross-linked free molecules to huge linkages (crystals) and second the crystals act as filled particles like carbon blacks in rubber. Thus the stress-upturn is reasonably revealed using the concept of the non-Gaussian chain, if we regard the molecular distance between crystals as the segment length between cross-links in the calculation of the non-Gaussian chains.

In the process of the stress-upturn in NR, two processes must be repeated, the slight stress decrease by the strain-induced crystallization and the following large stress increase by the finite molecular extension. Fig. 12 shows the stress–strain curves for various segment lengths (n) between cross-links (dotted lines) calculated based on the non-Gaussian treatment given by Kuhn and Grün [10]

$$\sigma = (\nu kT/3)n^{1/2}\left[L^{-1}\left(\lambda/n^{1/2}\right) - \lambda^{-2/3}L^{-1}\left(1/(\lambda n)^{1/2}\right)\right] \qquad (1)$$

where σ is the stress and λ the extension ratio and L^{-1} the inverse Langevin function and ν and n the number of network chains per unit volume and the number of the segments in a network chain respectively and k is the Boltzmann's constant and T the absolute temperature.

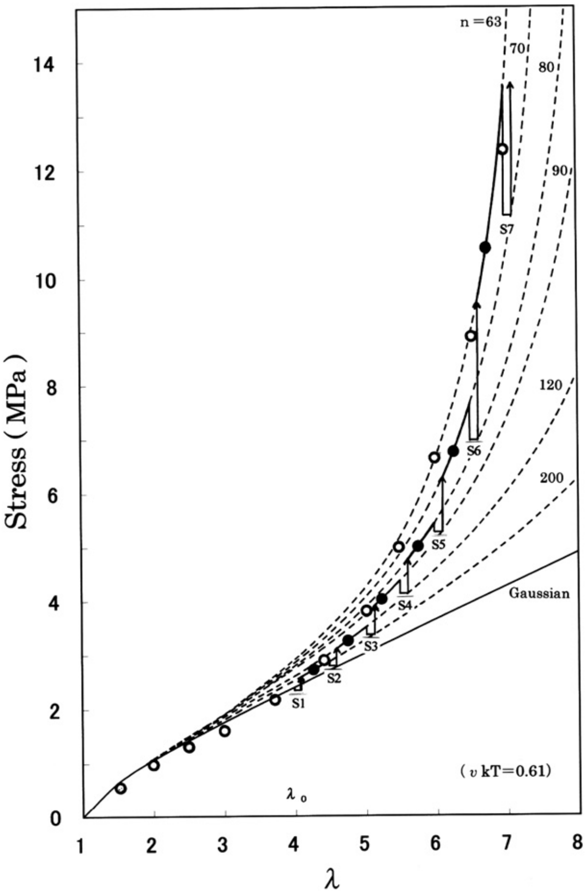

Fig. 12. Stress–strain curve of NR made through the step-up process (thick solid line).

The distance between crystals decreases gradually depending on the gradual increase of the crystals with increasing extension. Therefore, the stress–strain curve of NR must transfer the lines of different n value from large number to small one as extension increases in Fig. 12. The filled lines in Fig. 12 schematically shows the situation in the stress–stain relation, where the stress decreases first (crystallization) and increases thereafter (finite extension) passing through the step-up process ($s_1 \rightarrow s_2 \rightarrow s_3 \cdots s_6 \rightarrow s_7 \rightarrow$), going from one line to another. Filled circles in Fig. 12 correspond to the mean values in the each step, whereas open circles give the experimental results.

This treatment is basically different from the method that Treloar [9] performed, in which he revealed the whole stress–strain curve of NR using a single line with the fixed n value. Thus, of course, the stress–strain curve given by joining the filled circles in Fig. 12 shows the slightly steeper stress-upturn than that calculated with a single n value.

5.5. Strength of the super network constructed through the strain-induced crystallization

The general understanding for the self-reinforcement of NR, which is vaguely understood but widely accepted, is to assume such a morphological structure for the cross-linked NR after the strain-induced crystallization that the strain-induced crystals are well-dispersed and strongly adhered to matrix cross-linked rubber, as schematically shown in Fig. 13. Fundamentally, the model shown in Fig. 13 includes a serious error from a standpoint of the reinforcement of elastomers. In this model, the maximum tensile stress appears just apart from the surface of crystal in the matrix rubber, as shown in Fig. 11. It means that the matrix cross-linked rubber must support the very large stress concentration of the system under large extension, which is almost 25 MPa before rupture. However, the matrix cross-linked rubber itself (without crystals) behaves as the Gaussian chain and its tensile strength is only about 2–3 MPa as shown in Fig. 2. Thus, we can undoubtedly say that Fig. 13 model will give neither the stress-upturn nor the great tensile strength (25 MPa). Its tensile strength must be 3 MPa at most.

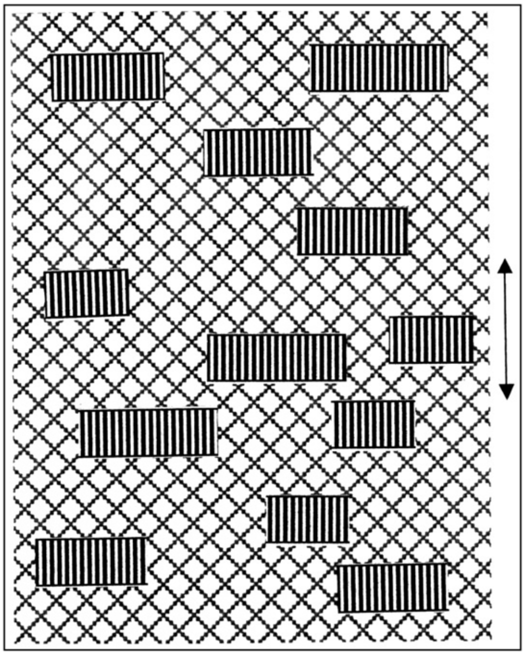

Fig. 13. Schematic representation of the conventional image for the crystal-filled vulcanized rubber.

Thus, the basic question will be what structure is newly constructed in the process of the strain-induced crystallization and supports such a large stress concentration of the system under large extension. In the case of the carbon black-reinforced SBR, the most important structure to support the great stress of the system is the continuous super network consisting of the strands of extended molecules interconnected at the carbon particles [5,7]. The continuous super network constructed through the strain-induced crystallization in the cross-linked NR shown in Fig. 10 is undoubtedly very similar to the continuous super network in the carbon black-filled SBR. That is, the continuous super network (Fig. 10) must support the very high stress of the system under large extension and generate the stress-upturn and the great tensile strength of the system. As a mechanical model, the stress field in NR is supported by the parallel contribution of the super network and the matrix rubber, where the super network is considered to support the stress of more than 90% of the total tensile strength of the system.

Now we roughly estimate the tensile strength (σ_B^0, true stress) of the super network given in Fig. 7 under the condition that the tensile strength (σ_B, industrial stress) and the extension ratio at break (λ_B) of the vulcanized NR at room temperature are 25 MPa and 9.0, respectively. In addition, we assume that the super network supports 90% of the stress of the system at break and the cross-sectional area of the Lx part in the cross-linked rubber in Fig. 8 is 0.1–0.2 in one direction. Thus, we can calculate the tensile strength (true stress) of the super network, σ_B^0 as 1–2 GPa $[= \sigma_B \times \lambda_B \times 1/(0.2-0.1) \times 0.9]$. This high value is almost the same as the tensile strength of the super-extended polypropylene fibre.

5.6. Mechanism of the stress-softening (Mullins effect) in NR

The highly oriented crystalline reflection peaks in X-ray measurement increases with increasing strain amplitude in loading and in the unloading process, the crystalline reflection still increases slightly when the strain begins to drop, then it decreases gradually with decreasing extension [23,27–29,45]. In contrast with this, although the stress increases with strain amplitude in loading, it drops abruptly just at the beginning of unloading and decreases gradually with decreasing strain. This means that the stress-upturn in loading is closely related to the amount of the strain-induced crystals, but the stress reduction in unloading is not directly connected to the amount of crystals.

The same stress-softening is observed and discussed in detail for the carbon black-filled rubber, where the author introduced the concept of buckling of the super network generated in the carbon black-filled rubber [5,7]. Here again, the author introduces the same concept for the mechanism of the stress-softening in the cross-linked NR. Fig. 14 represents the buckling of the super network in NR. Since the buckling occurs at the beginning of unloading and the buckled super network can hardly hold the stress of the system, the stress drops abruptly in the unloading, despite that the strain-induced crystals are still increasing at the beginning of unloading.

5.7. Mechanism of the carbon black reinforcement of NR

Finally, we consider the effect of filling with carbon black for NR vulcanizate. Generally, in the case of SBR, filling with carbon black generates a great increase in the tensile strength, more than 15 times, whereas NR is slightly reinforced by filling with carbon black, as shown in Fig. 1. That is, the unfilled NR is already almost on the same level as the filled NR in tensile strength. Furthermore as

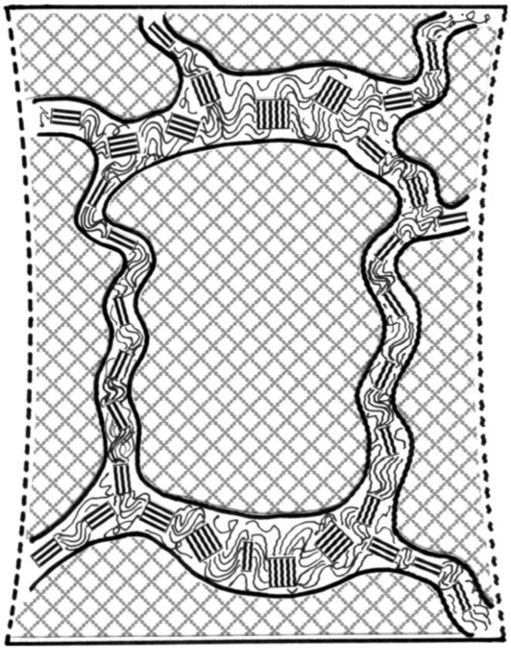

Fig. 14. Buckling of the super network in the vulcanized NR.

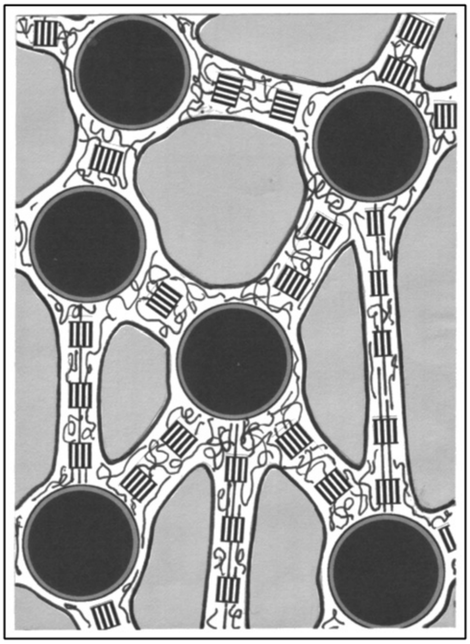

Fig. 15. Super network constructed in the carbon black-filled NR.

discussed before, in comparison between unfilled NR and filled NR, if we shift the stress–strain curve of the unfilled NR to a lower strain by a strain of 300–350%, it will coincide with that of the filled NR (and the filled SBR too), as shown in Fig. 1.

The carbon black reinforcement of SBR is fundamentally based on the formation of the continuous super network consisting of strands of extended molecules interconnected at carbon particles. In addition it is essential that the molecules in the bound rubber are not cross-linked even after vulcanization, which makes free sliding, orientation and finite extension of molecules possible. The same situation is realized in the case of the carbon black-filled NR. First, the bound rubber constructed around the carbon particles in the filled NR is kept in an uncross-linked state. Therefore, in the carbon black-filled NR, the strain-induced crystallization and the following finite extension of molecules take place mostly and preferentially within the bound rubber (under very large stress concentration, Fig. 11), which must be much faster than the crystallization in the matrix rubber.

Fig. 15 is a new model to represent the super network constructed in the carbon black-filled NR under large extension, in which the super network is revealed by double reinforced structures. That is, the strands of extended molecules interconnected at the carbon particles also consist of the extended molecules interconnected at the strain-induced crystals, i.e., double reinforcement for the system. The strain-induced crystallization, first and preferentially may occur within the uncross-linked bound rubber and later at a larger extension, it occurs slightly in the uncross-linked phase in the matrix cross-linked rubber. The reason why the strain-induced crystallization is accelerated in the bound rubber is that firstly, there are no cross-links in the bound rubber and secondly the very large stress concentration is generated in the bound rubber sandwiched between the hard carbon particles. Thus, the strain-induced crystallization will be able to take place at a much smaller strain in the carbon black-filled NR, compared with the case of the unfilled NR. An almost equal tensile strength (30–35 MPa) for the carbon black-filled NR and the carbon black-filled SBR (Fig. 1) shows that the tensile strength of the strand of molecules interconnected at the carbon particles is scarcely affected whether it includes crystals or not.

6. Conclusion

1) The author proposed a new model and concept that general unfilled rubber vulcanizates consist of heterogeneous structures, a partially continuous cross-linked phase (75%) and a continuous uncross-linked phase (25%).
2) The author also proposed other new models and concept for the strain-induced crystallization that the strain-induced crystallization takes place in the uncross-linked phase.
3) In the super network consisting of extended molecules interconnected at the crystals, the strain-induced crystals play a role to fix un-crystallized molecules, just like carbon particles in SBR. The stress-upturn is generated when un-crystallized molecules interconnected at crystals in the uncross-linked phase are finitely extended between huge linkages (crystals).
4) The super network supports a major part of the stress of the system, which is fundamentally in common with that given for the carbon black reinforcement of rubber, although there is the difference in the super network, whether it includes crystals or carbon particles.
5) Stress-induced crystallization occurs much faster by filling with carbon black. Strain-induced crystallization, first and preferentially occurs within the uncross-linked bound rubber surrounding carbon particles and later at a larger extension, it occurs in the uncross-linked rubber phase.

References

[1] Harwood JAC, Payne AR, Whittaker RE. J Appl Polym Sci 1970;14:2183.
[2] Thomas AG, Whittle JM. Rubber Chem Tech 1970;43:222.
[3] Gent AN, Zhang LQ. J Polym Sci Part B Polym Phys 2001;39(811).
[4] Guth E. J Appl Phys 1945;16:20.
[5] Fukahori Y. Rubber Chem Tech 2007;80:701.
[6] Fukahori Y. Rubber Chem Tech 2007;80:777.
[7] Fukahori Y. Nippon Gomu Kyokaishi (Japan) 2004;77:397. ibid, 77, 420(2004).
[8] Fukahori Y. Preprints in IRC-Yokohama; 2005, 28-G11-02.
[9] Treloar LRG. The physics of rubber elasticity. 3rd ed. Oxford: Clarendon Press; 1975. p. 101.
[10] Kuhn W, Grün F. Kolloid-Z 1942;101:248.
[11] Meakin P. Phys Rev Lett 1983;51:1119.
[12] Vilgis TA, Heinrich G. Angew Makromol Chem 1992;202/203:243.

[13] Folland R, Charlesby A. Polymer 1979;20:207. ibid, 20, 211(1979).
[14] Noguchi T. and Iwabuki H.: In the preparation for publishing.
[15] Fukumori K, Satou N, Kurauchi N. Nippon Gomu Kyokaishi (Japan) 1988;61:561.
[16] Noguchi T, Utsumi T. Nippon Gomu Kyokaishi (Japan) 2001;74:116.
[17] Ito M, Kaneshima K. Nippon Gomu Kyokaishi (Japan) 2003;76:81.
[18] Andrews EH. Proc Roy Soc. (London) 1962;A270:232.
[19] Andrews EH. J Polym Sci A-2 1966;4:668.
[20] Tsuji M, et al. Polym J 1999;31:784.
[21] Phillips PJ, Vatansever N. Macromolecules 1987;20:2138.
[22] Magill JH. Rubber Chem Tech 1995;68:507.
[23] Yau W, Stein RS. J Polym Sci A-2 1968;6:1.
[24] Trabelsi S, Albouy PA, Rault J. Macromolecules 2003;36:9093.
[25] Trabelsi S, Albouy PA, Rault J. Rubber Chem Tech 2004;77:303.
[26] Toki S, et al. Rubber Chem Tech 2006;79:460.
[27] Toki S, et al. Polymer 2003;44:6003.
[28] Murakami S, et al. Polymer 2002;43:2117.
[29] Tosaka M, et al. Macromolecules 2004;37:3299.
[30] Lee DJ, Donovan JA. Rubber Chem Tech 1987;60:910.
[31] Gent AN. J Polym Sci Part A-2 1966;4:447.
[32] Yau W, Stein RS. J Polym Sci Part B 1964;2:231.
[33] Mandelkern L. Crystallization of polymers. McGraw-Hill; 1964.
[34] Göritz D, Kiss M. Rubber Chem Tech 1986;59:40.
[35] Dohi H. Nippon Gomu Kyokaishi (Japan) 2007;80:86.
[36] Dohi H, Horiuchi S. Polymer 2007;48:2526.
[37] Nukaga H, et al. Nippon Gomu Kyokaishi (Japan) 2006;79:509.
[38] Watabe H., et al. Preprints in IRC-Yokohama; 2005, 28-G5-11.
[39] Iwabuki H. Nippon Gomu Kyokaishi (Japan) 2007;80:83.
[40] Fukahori Y, Mashita N. Polym Adv Technol 2000;11:472.
[41] Fukahori Y, Seki W. J Mater Sci 1993;28:4471.
[42] Wun KL, Prins W. J Polym Sci Phys 1974;12:533.
[43] Miyamoto Y, et al. Macromolecules 2003;36:6462.
[44] Tosaka M, et al. Macromolecules 2006;39:5100.
[45] Fiorentini F, Cakmak M, Mowdood SK. Rubber Chem Tech 2006;79:55.