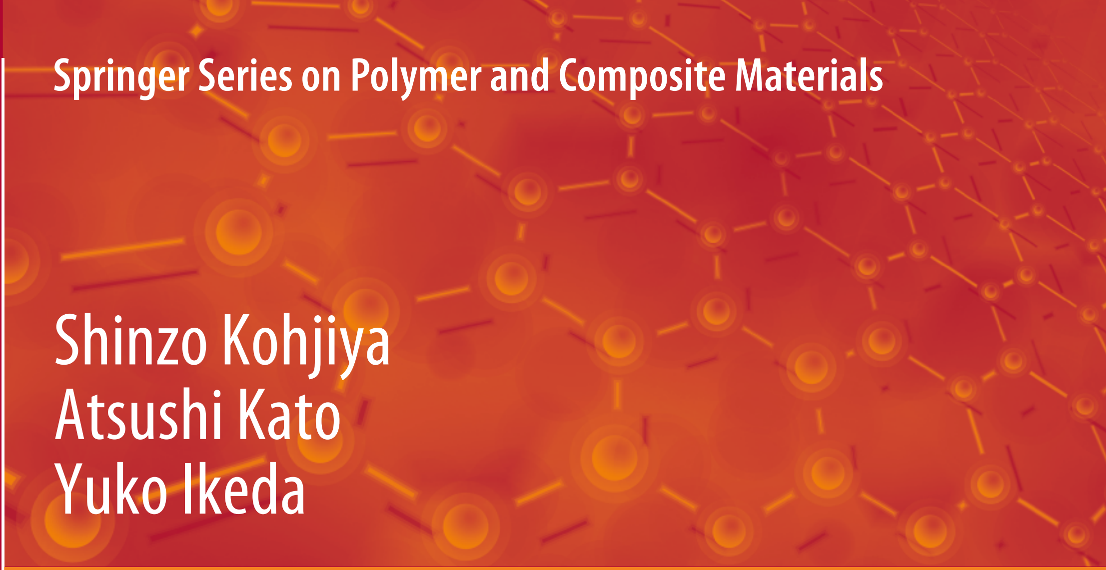

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Reinforcement of Rubber

Visualization of Nanofiller and the Reinforcing Mechanism

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Reinforcement of Rubber

Visualization of Nanofiller and the Reinforcing Mechanism

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Preface

This book is the most recent account on rubber reinforcement, highlighting nanofiller clustering in rubber matrix, in particular. It is needless to say that the rubber reinforcement has been recognized to be one of the most important research and developmental subjects among rubber chemists and engineers, together with vulcanization. On the one hand, the vulcanization is an indispensable precondition for rubber in order to make it serviceable as a stable elastic material. It was invented in 1839 by C. Goodyear when a rubber compound containing sulfur and white lead was by chance placed beside the heater which his wife, Clarissa, was using in the kitchen. This anecdote suggests that the kitchen was his laboratory, and he was not a professional technician but a poor backstreet inventor.

On the other hand, reinforcement of rubber by carbon black was reported by S. C. Mote in 1904 in the UK not as an invention but as a practice in rubber compounding process in combination with fiber cord, in order to manufacture automobile tires as a final product. In 1910, the Diamond Rubber Co. in Akron, Ohio, took out a license of this process, followed by the acquisition of the business by B. F. Goodrich in the USA. It is noticeable that the first mass-produced passenger car for ordinary people, i.e., Ford model T was commercialized in 1908. In accordance with the development of mass production of automobiles, the utilization of carbon black grew rapidly in the rubber industry, and black color soon became standard for tires.

Thus, due to the utmost technical importance of rubber reinforcement by loading carbon black, there have been published many, too many, technical reports and know-how to give a lucid and coherent explanation of reinforcing effect on rubber. In other words, the excessively abundant reports have failed to elucidate the exact reinforcing mechanism, which is to be of use in designing rubber compounds. Consequently, only one book entitled '*Reinforcement of Elastomers*' has been published so far focusing upon rubber reinforcement, in 1965. The book was edited by G. Kraus, and it has remained to be authoritative on rubber reinforcement for more than half a century. This surprising scanty of the dependable literatures of rubber reinforcement may be due to the extreme complexity of reinforcing mechanism, we have assumed.

The present book discloses a most recent trial to overcome this complexity by visualizing the three-dimensional (3D) image of nanofillers in rubber matrix, which has been enabled by applying a state-of-the-art technique using 3D transmission electron microscopy (3D-TEM), or alternatively called ‘electron tomography,’ to rubber/nanofiller composites. Through the analysis of 3D images displaying nanofiller dispersion, we have successfully visualized the aggregation state of nanofillers in rubber matrix, from which we suggest the formation of a unique semiflexible nanofiller network. This result is reasonably assumed to be the most important factor for rubber reinforcement by filler loading. In the case of cross-linked natural rubber, self-reinforcement effect (without any filler loading) upon stretching is effectively functioning, and a new polymer crystallization mechanism, template crystallization, is suggested for the strain-induced crystallization responsible for the unique self-reinforcement.

From the meaning of the word ‘reinforcement’ itself, engineering investigation based on fracture mechanics should be one of the approaches to the elucidation of rubber reinforcement. However, fracture mechanical studies on rubber materials have not been much successful so far, compared with those on metallic and inorganic materials. We hope that our results presented in this book may accelerate studies for establishing the fracture mechanical behaviors of rubber. In addition, reinforcement of rubber justifiably involves not only mechanical strength but also various functional properties: For example, the required functions of the tread rubber of pneumatic tires in driving include lots of dynamic properties such as traction, grip, rolling resistance, skid resistance, wear of rubber, and so on. Hence, only mechanically supporting the weight is absolutely insufficient for automobile and aircraft tires.

All these functional requirements make rubber reinforcement too complex to be fully elucidated by conventional techniques. The authors were fortunate to have an opportunity of applying a most recent nanometer visualizing technique, 3D-TEM, to nanofiller/rubber composites. Combined with the resultant 3D images of nanofiller in rubber matrix with both retrospective and prospective insights into rubber reinforcing mechanism, nanofiller structuring process to form the filler networks is elucidated by our studies. At the same time, well-known bound rubber, which is due to the rubber-to-filler interaction, is found to be involved in nanofiller networking and to play an important role of affording semiflexibility to the nanofiller network. This book is summarizing these studies, and the essential results disclosed here are expected to provide rubber engineers with a novel fundamental base for the scientific design of rubber reinforcement. The design would possibly contribute to the development of higher-performance rubber products in this century, which, we sincerely hope, might promote the sustainable development of transportation society further toward the next century.

Lastly, let us express our sincere thanks to many people to whom we have owed much in experiments and discussions, in particular to the students at Kyoto Institute of Technology and the coworkers at NISSAN ARK CO.

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Part I
Filler Reinforcement of Rubber

Chapter 1
Rubbery Materials and Soft Nanocomposites

Abstract Rubbers are to be vulcanized and reinforced for their applications. Vulcanization is the most important prerequisite for displaying a stable rubber elasticity for practical utilization, while rubber reinforcement is to meet the demands of practical uses in terms of mechanical and some other functional requirements. Among lots of ingredients for rubber compounding, carbon black (CB) was found to afford several crucial characteristics for rubber tires as well as mechanical strength, early in the twentieth century. Since then, CB has been the most important filler for rubber industry, and the natural rubber (NR)-CB combination pioneered a new concept, polymer composite, together with the use of the rubber/fiber composition. This chapter gives a highly scientific but still general introduction to rubber reinforcement by means of filler. Traditional approaches are briefly described, too, from a retrospective point of view, which are expected to afford an excellent base for a modern approach to rubber reinforcement in this century.

Keywords Vulcanization · Reinforcement of rubber · Filler · Carbon black · Nanocomposite

1.1 Introduction to Rubber Reinforcement

The rubbery material, which we generally note in our everyday life, is actually a rubber vulcanizate, i.e., a chemically cross-linked rubber [1–4]. We are reasonably assuming that the vulcanization, or the cross-linking in general, is a precondition for raw rubber to make it serviceable as an elastic solid material, except a few special cases, e.g., rubber adhesives (technically a solution of uncross-linked rubber). In addition, we assume that many rubber products are containing carbon black (CB), since we observe most of them being black in color, typically when seeing the tires of aircraft, automobiles, and bicycles daily. Thus, we generally acknowledge the carbon black-loaded rubber vulcanizate as 'rubber.'

Above observation suggests us that the vulcanization of rubber to form a three-dimensional (3D) rubber network structure and the CB mixing in rubber for the purpose of reinforcement are the two essential issues for rubber as a stable elastic material of use, and they have been the central subject in rubber science and in its

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applications [2–12]. We are now living in a transportation society [1, 3], and we often watch pneumatic (i.e., pressured air-filled) rubber tires, the rubber components of which are reinforced with CB as well as cross-linked. The two outstanding technical issues of rubber would remain to be of utmost importance to the end of this century, or well into the twenty-second century [3, 12] (see also Chap. 9 of the present book, for rubber reinforcement from the viewpoints of globalization and sustainable development).

Here, a retrospective view of the relationship between CB and rubber is given at first: This combination has incidentally suggested certain compatibility of CB with rubber to afford an interesting reinforcement effect on rubber vulcanizates. Unique rubber elasticity, a mechanical property of rubber, is found to provide us with several functional properties in practice, when applied to rubber tires [1–3, 8, 12]. Namely the functional property of top tread rubber of tires includes lots of dynamic properties such as traction (transmission of driving and braking forces to the road surface), grip of the road surface, rolling resistance, skid (movement of tire under no rotation) resistance, wear of the contacting rubber layer on the road surface, and so on. These are not much related to mechanical strength but more or less to friction (both dynamic and static) and abrasion/wear phenomena. Both interestingly and importantly, the compounding of CB into rubber enables us to control these indispensable properties of tire rubber as well as mechanical properties. In consequence, ‘reinforcement’ of rubber is not simply relevant to mechanical issues, but to several dynamic and functional properties controlling the driving capability of automobiles. This is an outstanding difference from the reinforcement of polymer by a composite formation in general.

Additionally, the affinity of rubber with CB as mentioned above has been found in other nanofillers, e.g., particulate silica. Hence, the specific functional performance of rubber vulcanizates compounded with nanofillers has been recognized among rubber scientists and engineers for long. It is notable here that nanoparticles, including CB and particulate silica, have relatively huge surface area, and the interaction between two nanoparticles is very strong. Consequently, they are destined to cluster each other due to the Van der Waals force. The nanofiller-loaded rubber vulcanizate is to be regarded as a representative soft nanocomposite to be a material of choice for pneumatic tires in the present transportation society [3, 12], which is more detailed in the later chapters.

With such perspective and prospective views, this chapter is going to give a general introduction to the main parts of this book on rubber ‘reinforcement.’

1.2 Carbon Black-Loaded Natural Rubber Vulcanizate: The Pioneer of Polymer Composite

The industrial manufacturing of the soot is originated from Hydro Carbon Gas Black Co. in 1872, which commercialized it under the name of ‘Carbon Black.’ They used natural gas as the starting material (traditionally, pine trees have been employed for soot), and the sale of their product by the channel method experienced a sudden increase in the 1910s. What happened, then?

Early in the twentieth century, the CB-loaded vulcanizate of natural rubber (NR) was reported by S. C. Mote (1867–1944) to be of value in manufacturing a rubber tire in combination with fiber materials [13]. His patent in 1904 (to Silvertown Co. in England) referred to the use of CB and NR mixture, but its main claim was not on CB/NR mix but on NR composites with a fiber cord for automobile tires. In 1910, the Diamond Rubber Co. of New York, whose factory was at Akron, took out a license to manufacture and sell this tire in the USA. This business was acquired in 1912 by B. F. Goodrich, who later sponsored a full-page advertisement (Boston Sunday Post, May 14, 1916) as follows:

> Without the strength, endurance and enormous mileage-power of these genuine Silvertown Cord Tires, the recent racing speed for 350 miles of 102 miles per hour average, would have been impossible.

The Cord Tires which were manufactured from CB/NR mix combined with fiber cords did give rubber tires of excellent performance as advertised [13]. Here ‘two new factors’ may be recognized in the rubber composite: First NR was mixed with CB, and secondly, the rubber mix was further combined with fiber cords. The first has afforded excellently reinforced NR compounds, which is the origin of rubbers compounded with CB or any other nanofiller in general. The selection of CB, in particular, by Mote was a uniquely amazing finding. Even though there had been tried so huge number of additives, both inorganic and organic, since the invention of vulcanization by Goodyear in 1839, CB had not been much mentioned specifically. Goodyear himself was one of such inventors to find sulfur a key material: Note that he did not think the vulcanization was a chemical reaction at all. It was quite possible that someone had tried CB mixing into rubber before Mote, but had failed to recognize any specific affinity of CB with rubber.

Mote’s selection of CB might suggest his insight into the nature of rubber; rubber is apparently solid, but it is liquid-like due to the segmental micro-Brownian movement of rubber [3, 12, 14]. In mixing a solid (CB) into a liquid (rubber), affinity or compatibility between the two is an important factor to get a good solution. H. J. Stern, the author of Ref. [13], checked the CB content of the remaining Mote’s original rubber compound, and reported that it was 23%. This value is approximately comparable to 30 phr of CB, which is the range still used in many rubber formulations (The phr designates parts per hundred rubber by weight.). The CB used by Mote was a channel carbon (the words ‘gas carbon’ is also used, since natural gas is the raw material), not a furnace carbon. But, the difference of their specific gravity is not so much to negate the semiquantitative comparison shown above. CB has still remained the prime reinforcing agent in the rubber industry. His finding has given us the first part of the standard rubber formulation rule, i.e., selection of a suitable filler at the first step, which has much helped rubber engineers in their design of rubber products, so far.

In addition, Mote's achievement might be strengthened by the efforts of G. Oenslager (1873–1956) at Diamond Rubber Co. He was pioneering the use of organic accelerators in combination with sulfur for rubber vulcanization [15]. It is well known that the development of sulfur cross-linking (i.e., vulcanization) technique has been in close mutual correlation with rubber reinforcement [2–12, 15]. For instance, the shift of CB from gas carbon (manufactured by the channel method) to furnace carbon (manufactured by the furnace method established in the 1940s: HAF and ISAF are the representative grades) in rubber industry was followed by the change of organic accelerators to the delayed-type ones, too. Recently, a new mechanism of the vulcanization reactions is reported [16–21], and if this mechanism is found to be exactly the case, some features of rubber reinforcement are going to be modified accordingly. From the scientific point of view, reinforcement and vulcanization are independent, but in practice the two are mutually related in the arena of rubber processing technics.

The second factor, idea of combining rubber with a fiber material, commonly called a tire cord, has been applied and practiced in polymeric materials as well as in rubber industry. Among them, fiber reinforced plastics (FRP) is now widely known as an example of composite material [22]. In other words, demand for pneumatic rubber tires has provided us with an innovative new soft composite of much higher performance from polymer and fiber, too. In rubber processing, the two pairs, i.e., rubber/nanofiller and rubber/fiber cord have been skillfully combined, which has been an essential technical core in rubber manufacturing industries until the present time. Rubber tires and rubber belts are typical examples.

The pneumatic rubber tire is an elastic device, i.e., a soft container of the pressured air, supporting automobiles or aircraft on the road surface [1–3, 11]. Mechanical strength enough to support a heavy object such as the automobile or airplane is obtained in combination with fiber materials. On the other hand, the effects of compounding CB into rubber are not limited to mechanical properties [2, 3, 11, 17]. In addition to mechanical strength, the function of top tread rubber of tires, which is always in contact with the road surface, suggests much more complex yet amazingly lucid features during driving (in the case of aircraft, also taxying), that is, traction, grip, high skid resistance even under rainy conditions, low rolling resistance, appropriate abrasion or wear of their surface in touch with the road surface, deterrence of hydroplaning when driving under rain at a higher speed, and so on.

Separately from those, heat buildup is a big challenge for tire rubbers from a chemical point of view. When driven, tires are under high-speed rotation on the road surface, which results in much heat generation due to dynamic friction leading to heat buildup of the tire. The temperature increase of the tire has to be arrested by the dissipation of heat due to air cooling. During driving, the competition of two factors, heat by friction and air cooling, results in an equilibrium temperature of tire, which is to be as low as possible, of course, for the safety driving and longer lifetime of tire rubbers. Note that this equilibrium temperature has to be absolutely lower than the melting temperature of fiber cords used in the tires. The temperature may be highly dependent on lots of internal structural details as well as the thermal stability of used materials. In addition, external conditions matter, which include driving conditions (driving speed, duration time of the speed, etc.), climate conditions (atmospheric temperature, rainy or not, windy or not, etc.), and surface conditions of the road. From viewpoint of the tire design, the heat resistance of all the materials used in the tire is to be checked first, and many structural issues, particularly, the assembling mode, and how to form composites in tire construction of all the parts [2, 3, 23]. For example, radial tires are said to be easier to design the lower heat buildup than bias tires, which was one of the reasons of the bias-to-radial transition in the worldwide tire market.

While the fiber cords provide the tires with mechanical strength to support the body of automobile or airplane, many of the important functions of tire rubber on the road surface have reasonably been controlled by the insightful utilization of CB mixing with rubber. Good rubber mixing technique, particularly with CB, has been the central issue of importance among rubber engineers and is still one of the most decisive issues in rubber processing technique. At the same time, rubber mixing remains to be much dependent on technical skillfulness of rubber engineers working on rubber processing, and more scientific rationalization is urgent in order to make a design of rubber mixing more rational and more systematic [3].

In any way, tires have to support the body of the automobile, truck, and even aircraft, and to display friction and abrasion-related functions on the road surface, with mandatory need to be driven in safety even under a high-speed movement. In the case of aircraft, too, taking off for flight and landing after flight are essential, and the aircraft tires have to endure the extremely harsh conditions for organic materials. Including taxying between the gate and the runway, the safety issue of aircraft running is the most crucial and critical issue for airplanes in making a flight, hence the aircraft tires are to be under a close examination before and after each flight.

In the processing stage, CB-mixed NR compound is stretched on fiber cords, and the composite is vulcanized in the metallic mold to give a final product, which is often called a soft composite. FRP may be a soft composite when compared with ceramic or metallic materials [22] but FRP is not elastic. Nearly one hundred years later from the rubber composites, FRP is recently used for automobiles as the body materials [24] More recently, graphene is focused as filler for rubber [25, 26]. Nanocarbon fiber, graphene, and CB are all carbon allotropes, and the use of them is expanding not only as a filler for mechanical improvement but also for the functionalization of material. This trend may be against the decarbonization trend, which is advocated against the progress of global warming due to a few carbon compounds, e.g., carbon dioxide. However, some carbon allotropes are too good to abandon, and CB is surely one of them, and graphene, too.

Here, one famous monograph on rubber reinforcement is specifically to be mentioned: *Reinforcement of Elastomers*, edited by G. Kraus and published in 1965 [5]. This book is a collection of dependable reviewing chapters at the time and has been read and referenced extensively until now. Unfortunately, however, no such books have appeared since then. While reading the present book, it is often beneficial to return to this semilegendary reference nowadays: Following are the chapter titles and their authors for your reference.

Chap. 1	Network Theories of Reinforcement, F. Bueche
Chap. 2	Mechanism of Tearing and Abrasion of Reinforced Elastomers, S. D. Gehman
Chap. 3	Dynamic Properties of Filler-Loaded Rubbers, A. R. Payne
Chap. 4	Interactions between Elastomers and Reinforcing Fillers, G. Kraus
Chap. 5	The Nature of Polymer-Filler Attachments, J. Rehner, Jr.
Chap. 6	Microscopy in the Study of Elastomer Reinforcement by Pigment Fillers, W. M. Hess
Chap. 7	Rheological Behavior of Filler-Reinforced Compounds, C. C. McCabe
Chap. 8	Chemical Interaction of Fillers and Rubbers during Cold Milling, W. F. Watson
Chap. 9	Promoters of Filler Reinforcement, J. O. Harris and R. W. Wise
Chap. 10	Commercial Manufacture of Carbon Black, O. K. Austin
Chap. 11	Latex Masterbatching, J. H. Carroll and R. N. Cooper
Chap. 12	Compounding with Carbon Black, M. L. Studebaker
Chap. 13	Reinforcing Fine Particle Silicas and Silicates, J. W. Sellers and F. E. Toodner
Chap. 14	Properties of White Reinforcing Fillers in Elastomers, H. Westlinning and H. Fleischhauer
Chap. 15	Reinforcement of Rubber by Organic Fillers, O. W. Burke, Jr.
Chap. 16	Reinforcement of Polyethylene by Carbon Black, B. B. Boonstra
Chap. 17	Antioxidant Properties of Carbon Black, W. L. Hawkins and F. H. Winslow.

1.3 Reinforcement of Cross-Linked Rubber by Particulate Nanofiller

As mentioned, CB-loaded NR vulcanizate, which was a pioneer of polymer composites, became so popular that it was simply expressed as ‘rubber.’ This situation began to change, however, during the World War II: Both in USA and in Germany, mass production of synthetic rubber was established. After the war, a few synthetic rubbers were commercialized, and among which styrene-butadiene rubber (SBR) became very popular as a rubber component of tires. Utilization of SBR continued to increase, and CB-loaded SBR vulcanizate was as important as that of NR. Nowadays, ‘rubber’ is a collective noun inclusively expressing NR, SBR, and many other synthetic rubbers [3, 7, 9, 27].

The growth of SBR was once so great that some rubber people even predicted the complete substitution of NR by SBR in the near future. When one of the authors (S. K.) started his study on rubber late in the 1960s, the initial assignments to him included the synthesis of new rubbers by cationic polymerization technique and a test of new type SBR. Hence, his career on rubber started by the research on synthetic rubbers. However, both unique and excellent properties of NR have enabled NR to survive through the avalanche of synthetic new rubbers, and during the past several decades its share in the rubber market has kept 40% or above, and it is predicted that it could be over 50% in the near future.

In this era of coexistence of NR and synthetic rubbers, CB consumption in rubber industry is continuously increasing, since the CB mixing is of more necessity when using synthetic diene rubbers such as SBR, NBR (acrylonitrile-butadiene rubber), and CR (chloroprene rubber) than in NR. Specifically on the comparative reinforcing effect of CB on NR and SBR, see Fig. 8.7 in Chap. 8. Predominance of CB in rubber reinforcement is expanding with the increase of synthetic rubber usage. Accordingly, even after the arrival of synthetic ones in the rubber market, many of rubber products are CB-loaded rubber vulcanizates, and they are now recognized simply as ‘rubber’ by the general public.

Recently, the use of particulate silica is increasing in addition to CB. It is sure that silica shows some characteristics superior to CB, but a few outside factors are involved: The source of CB being petroleum has been proved to be problematic, since the production of petroleum is much localized and is believed to be exhausting. In fact, ‘decarbonization’ is a trend in this century. On the other hand, the source of silica is abundant everywhere on the earth. Also, silicon chemistry has a long research history both in organic and inorganic arenas [28], and silicone elastomer is occupying an important position among specialty rubbers. Particulate silica of nanometer radius is available, and it is applicable to not only silicone rubber but many other rubbers including NR and SBR. Hence, silica is alternative to CB for a rubber reinforcing nanofiller, and lots of technical studies are reported up to now. Compared with CB, surface modifications of silica particle are much easier, and utilization of silane coupling agents has been one important area of studies in rubber reinforcement [29–34]. Chapter 7 is dedicated to silica reinforcement.

1.4 Development of Soft Nanocomposite

Manufacturing and consumption of the CB-loaded NR vulcanizate have been more than satisfactory, even after the introduction of synthetic ones as described in the previous subsections. Further, rubber composites from the rubber mixed with nanofiller are soft, i.e., highly stretchable and recoverable to afford the repeated stretching. These unique features, which are the characteristic of rubber elasticity [1, 3–5, 8, 11, 35–38], have enabled them to survive through the Era of Nanotechnology [39, 40]. In a sense, the use of nanofiller for rubber composites has been quite common, and we do not need to use the word ‘nano,’ since the rubber reinforcing filler was well recognized to be a nanosize particle even before 1960s [5], which is to be discussed more in Chapter 2. Among lots of fillers for rubber, nanofillers whose radii are of several or a few tens nanometers including CB and silica have been in conventionally used in rubber industry all over the world. This book is concerned mainly on rubber reinforcement mechanism, not aiming an exhaustive account on rubber reinforcement. Therefore, CB and silica are under consideration here. The two have been