CHARACTERIZATION OF BIPHASIC STRUCTURED NATURAL RUBBER/*IN SITU* SILICA COMPOSITES

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GENERAL INTRODUCTION

The term “rubber” describes a group of materials, which are excellently elastic: a strip of rubber can be stretched several fold without breaking and will return quickly to its original length on releasing the stretching force. This property of rubber elasticity originates from the fact that all rubbers are composed of long, flexible molecules [1,2]. Among various types of rubber, the most well-acknowledged and indispensable rubber is natural rubber (NR) due to its outstanding properties to cover a wide area of applications [3-5].

NR is known as a latex product from a certain type of the tree, i.e., *Hevea brasiliensis*. NR latex was the first latex to be used industrially. The *Hevea brasiliensis* tree was originally found growing in the Amazon region of South America. Since the later part of the 19th century, this three has been growing extensively in plantations in others tropical regions of the world, notably in South East Asia [3-7]. In an early state in industrialization of NR, various forms of solid dry NR was required to produce by the manufactures in developing rubber industries countries. The lack of interest in NR latex as a raw material, on the other hand, was due to an inability to preserve NR lattices against spontaneous coagulation [6,7]. As NR latex is the sap of a specialized type of cells in the *Hevea brasiliensis* tree, namely, the latex vessels, it is a complex biochemical system. It is therefore not surprising that obvious chemical changes occur shortly after the latex leave the tree. However, Norris [8] and Johnson [9] had solved this trouble by establishing patents to use ammonia as a standard preservative for NR latex. It was therefore possible to transport the latex long distance from the tropical regions in which it was produced to customers in many regions without serious concomitant deterioration.

Since then, both latex and solid products of NR are regarded to own a unique place in rubber technology due to its excellent green strength compared to other synthetic rubbers. However the strength of NR is not especially strong and stable as a spring metallic. Thus necessary properties are imparted by contriving to cross-link the long molecules by the process of cross-linking. However, it is recognized that the performance of vulcanized NR for many applications is enhanced by the presence of nano-fillers. Carbon black has been used since the early 1900s to reinforce rubber materials [10-12]. An important aspect of the reinforcement by active fillers has been believed to be due to the dispersion of filler particles in rubber matrix. It is also well known that primary CB particles are ideally wetted by rubbery matrix [13]. In facts, however, CB particles are mutually fused to form large particles called “aggregates”, since manufacturing process of CB. The aggregates further cluster into higher order structures called “agglomerates” when they are dispersed in rubber matrices.

More recently silica has been used as a filler in rubber. Silica was not originally classified as a reinforcing filler because silica-reinforced rubbers exhibit much lower mechanical properties, particularly lower tensile strength at break point and poor abrasion resistance when compared with carbon black-reinforced rubber. Silica was initially used in addition to carbon black.

The inferiority of silica, compared to carbon black, is best demonstrated by its poor processability, conventionally carried out by mechanical mixing, followed by heat molding under pressure. Incorporating silica into rubber has been considered more difficult than carbon black due to its polar surface resulting in a strong filler-filler interaction and thus filler aggregates. Silica is less compatible with rubber and harder to be dispersed well by mechanical mixing.

Two major breakthroughs have transformed conventional silica into a reinforcing filler that can achieve several properties of carbon black fillings. In particular, a decreased hysteresis is of major interest for tyre applications. The first step was made in the 1970s by Wolff, who proposed a specific silane coupling agent, TESPT (bis(triethoxysilylpropyl)tetrasulfide) [14]. Since this development, the utilization of silica has generally required coupling agents composed of sulfur functional organosilanes to chemically modify silica surfaces and promote interaction between hydrophilic silica surfaces and the hydrophobic rubber phase, as schematically shown in Figure 8.1. In order to understand the coupling mechanism of the silane coupling agent (i.e. TESPT), various kinds of analytical techniques, such as ^{29}Si-CP/MAS solid-state NMR [15], bound rubber analysis [16,17], X-ray photoelectron spectroscopy [18], gas chromatography [19], high-performance liquid chromatography [20] and energy-filtering transmission electron microscopy (EFTEM) [21] have been used. Among these techniques, EFTEM has very reliable results that characterize the local chemical structures of materials by combining electron energy loss spectroscopy (EELS) [22,23]. EELS analysis can be used for elemental mapping of Si and S, which provides information on the formation of the interfacial coupling layer of TESPT between silica and rubber [23].

Nowadays, it is well known that coupling agent technology reduces the problem of filler–filler interaction and thus the Payne effect [24-26], and so the use of silane coupling agents has been expanded widely in the rubber industry. However, this coupling system is considered to be expensive relative to carbon black-filled systems, so it was proposed to use the second step which emerged in the 1990s, as seen by R. Rauline’s patent [27]. In combination with the TESPT technology, this patent introduced the use of specific precipitated silica to achieve a reinforcement effect. The patent contributed to Michelin’s ‘Green Tyre Technology’, which was invented to reduce rolling resistance and hence fuel consumption. It also boosts silica consumption and led to a significant development in silica/rubber technology, as the large-scale replacement of carbon black by silica in tyre compounds has been realised since then. The silica/silane technology has been used widely in both academic and industrial works. However, there are still problems regarding the dispersion of silica in rubber matrix and also in terms of energy consumption in preparing the compound mechanically, which is much larger than that of the carbon black mixture. In order to solve these problems, therefore, not only was a method of improving the compatibility of silica surfaces and rubber as noted above discussed, but a technique to generate very fine silica particles in rubber matrix was also researched during the same period.

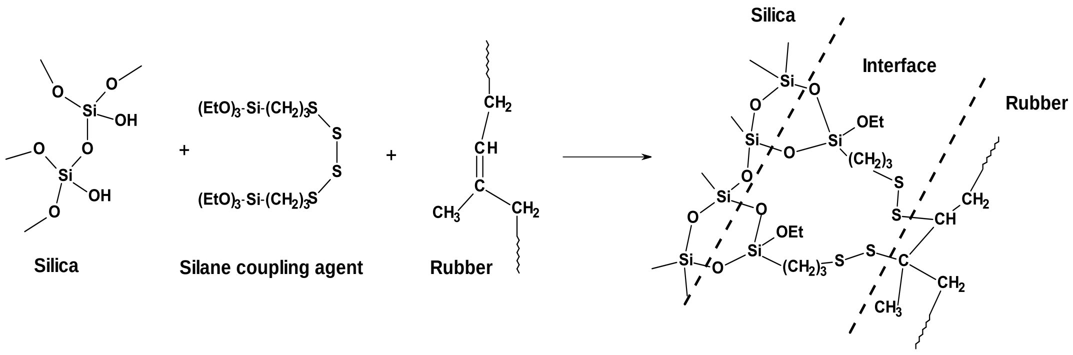

Figure 2 Schematic illustration of the coupling reaction of TESPT in a silica/rubber composite at the interface between the silica and the rubber.

A sol-gel method was developed as a novel method for improving the dispersion of the particulate silica by generating the silica in the rubbery matrix [28]. For example, the sol-gel reaction of tetraethoxysilane (TEOS) to generate silica as shown below:

$$Si(OC_2H_5)_4 \quad + \quad 2H_2O \quad \rightleftharpoons \quad SiO_2 \quad + \quad 4C_2H_5OH$$

This reaction occurs in rubber matrix. Therefore silica is often called as "*in situ* silica". In the last two decades, a development of in situ silica filled rubber matrix has been intensively studied using various kinds of rubbers [28-68], especially in a swollen state. Whilst there was a claim about the limitation in swelling of rubber sheet, in situ silica content up to 80 parts per one hundred rubbers (phr) was reported to be successfully synthesized in NR matrix [52-53]. The later generation of in situ silica filling rubber was focused on the utilization of rubber latexes, because the better dispersion of the in situ silica is expected by using the latexes.

There have been a few studies on the sol-gel method to generate in situ silica from alkoxysilane in rubber latexes [57-61] including NR latex. In these studies, however, the latex was coagulated to obtain the rubber-silica masterbatch in solid state, followed by mixing curing reagents by use of a conventional mechanically mixing technique

[57-61]. The compounds were then subjected to cross-linking process to afford silica filled rubber composites by compression molding. The formation of in situ silica in rubber latex is one of the new candidates to produce new composites, but the following processing techniques were still trivial. Additionally, the amount of silica introduced by the sol-gel reaction was not high due to a destabilization of latexes. The destabilization resulted in a coagulation of latexes and precipitation of solid rubber when a high content of inorganic precursor was added. According to the difficulties in preparing in situ silica/rubber latex composite discussed above, the study on preparation of in situ silica/NR composites prepared from NR latex was carried out previously [68]. In the present work, some important characteristic of the composites were investigated in order to better understanding its structure-properties relationship.

Among various types of rubber, on the other hand, NR is the most typical one and an indispensable material for many applications. The versatility of NR is mainly due to its outstanding tensile properties and good crack growth resistance, which originates in its ability to crystallize upon elongation [1-4]. Thus, a study on the strain-induced crystallization (SIC) in cross-linked NR is a significant subject from both academic and industrial viewpoints.

This ability to crystallize under strain is often explained by the high regularity of the macromolecular structure, i.e., its percentage of chains being in cis-configuration, which is very close to 100% in NR. Synthetic isoprene rubber (IR) exhibits a lower crystallinity than NR because of the lower regularity of the macromolecular structure, even though it can contain more than 98% of chains in cis-configuration [1-4].

Additionally, some authors also argue that the non-rubber components in NR (6 wt. % of proteins and lipids) play a major role in its excellent mechanical properties, because they enhance its capacity to crystallize [70,71].

SIC was discovered in 1925 by Katz [72], who was the first to show the x-ray diffraction pattern of a uniaxially stretched NR. Note that unstrained NR can also crystallize by cooling; this phenomenon is called thermally induced crystallization (TIC), or “cold” crystallization and was studied for example by Bekkedahl and Wood in the 1940 [73,74]. After the discovery of Katz, a large number of WAXD studies were performed especially during the 1930s and the 1940s. Some of them were dedicated to the crystal structure of NR, but rapidly some engineering studies investigated more deeply SIC of NR. In the last decade, this topic has been updated by the use of synchrotron radiation, which permits to perform real-time experiments. In this study, experimental setup of simultaneous WAXD and tensile measurement is displayed in Figure 3.

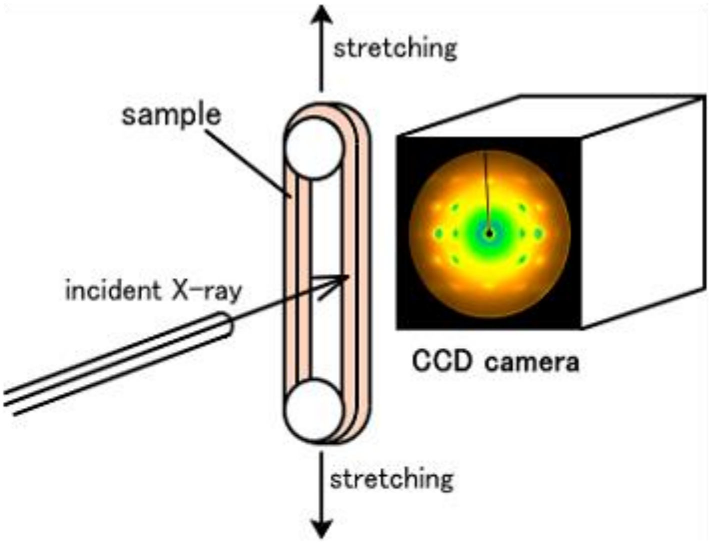

Figure 3 Experimental setup of simultaneous WAXD and tensile measurement.

The crystal structure and the lattice parameters of strain-induced crystallized NR can be deduced from the x-ray diffraction pattern. Figure 5 gives a typical example of a diffraction pattern that can be obtained when x-ray beam is perpendicular to the stretched sample.

Among the most intense diffraction spots, one can distinguish the ones that are due to crystallographic planes (200), (120), and (002). The position of the spots gives the distance d_{hkl} between (hkl) planes, by using the Bragg's law

$$d_{hkl} = \frac{n\lambda}{2\sin\theta}$$

where n is a strictly positive integer, λ is the wavelength of the x-ray, and θ is the diffraction angle (or Bragg's angle) of the spot due to (hkl) planes.

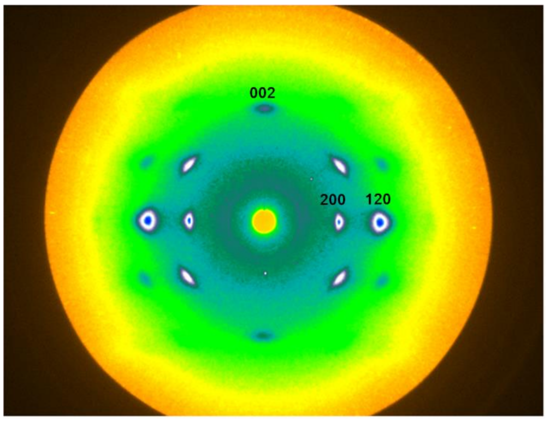

Figure 5 Typical WAXD pattern of a vulcanized NR stretched up to 9.25 times its original length; the stretching direction is vertical.

As mentioned previously, the study on SIC behavior by simultaneous tensile and WAXD measurements is being focused among rubber scientists. Many factors were reported to affect on SIC behavior of NR, for example, cross-linking density, filler loading.

Studies on effect of filler on SIC behavior of NR matrix were also reported from many aspects. Among these reports, there is one common observation was reported. By introducing reinforcing filler into rubber matrix, onset of crystallization becomes smaller [75-83]. Therefore, a common conclusion on this phenomenon is made: The smaller onset strain of SIC of the reinforced systems is ascribed to the decrease of the volume fraction of rubbery phase at first and to the high interfacial interaction between reinforcing fillers and rubbery matrix. The former is a volume effect in general when filled. The latter is dependent on the kind of mixed filler. Especially, when reinforcing filler use used, the onset strain tends to be smaller as the interfacial interaction between reinforcing fillers and rubbery matrix would become higher than the non reinforcing filler.

In this study, the in situ silica/NR composite is expected to have the strong interfacial interaction and also specific morphological feature is observed. Therefore, some important characteristics of this material would be disclosed in this study by conducting SIC analysis

Chapter 1 of this thesis, development of particulate silica generated in situ in NR matrix is reviewed for the better understanding in the characteristic of in situ silica/NR composites which can be obtained by various technique. Each technique has its own advantages and nature of sol-gel reaction is found to be difference among them. This study is focused on the technique that the sol-gel reaction is progressed in NR latex and formed the sample by casting technique. As a result, an intrinsic morphology of the sol-gel reaction in NR latex can be observed. Later, the observed morphology is named as “biphasic-structured composite”

Chapter 2, a morphological feature of in situ silica/NR composite which prepared by soft processing technique is reported together with mechanism of the formation of biphasic structure. The formation of biphasic structure is regarded as one of the important aspects of this thesis. Therefore, in Chapter 2, the author had primarily subjected the samples to dynamic mechanical property analysis. As a result, relationship between the forming biphasic structure and dynamic mechanical properties is clearly disclosed in Chapter 2.

Subsequently, in Chapter 3, effect of the biphasic structure on SIC behavior of NR is presented. As discussed above, an outstanding properties of NR is derived from SIC behavior. By forming the biphasic structure, it is thus believed to bring about a specific SIC characteristic of NR. Therefore, the author aimed to enclose an effect of unique morphology of composite by means of SIC study in Chapter 3. The obtained results suggest that the biphasic-structured composite composts of larger and smaller sizes of in situ silica networks. The difference in size can be ascribable to the original bimodal size distribution of NR latex [7] that worked as a template of biphasic morphology. Due to the difference in filler network size, in situ silica networks are found to be heterogeneously deformed as noticed by SIC analysis.

The formation of in situ silica network was thus considered to be useful for revealing of role of filler network on SIC of NR matrix, served as Chapter 4. In the society of rubber science and technology, reinforcing filler owns a large area of research among rubber scientist as its mechanism in reinforcement is not well-clarified. Among various theories of reinforcement, the formation of filler network is often used to explain specific mechanical properties such as Payne effect [24-26] and Mullins effect [84] in rubber-based composite. Unfortunately, so far, there was no such appropriate model sample for intensively and correctly revealing the role of filler network. By taking an advantageous of solution mixing and casting processes, in situ silica network can be achieved. This in situ silica/NR composite is believed to be the most suitable model as rubber matrix which covered by in situ silica network is purer than the conventional sample which obtained by milling.

In Chapter 5, the author found out that even after milling process, still the in situ silica/NR composite shows an excellent reinforcement behavior as monitored by SIC analysis. This is also an important aspect of this material as SIC results can be suggests the strong interfacial interaction between in situ silica and NR matrix.

Based on these contents, this thesis introduces a new kind of rubber-based composite which obtained from NR latex by utilizing NR particles as a template. The preparation technique here is found to be very simple but has advantageous in various ways, especially for revealing the role of filler network as mentioned above. The author wishes that this thesis would contribute to the development of rubber science and technology.

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CHAPTER 1

Chapter 1

Recent advances in particulate silica in natural rubber generated *in situ*

1.1 Introduction

Using the premise that excellent reinforcement can be achieved when very fine silica particles are incorporated and dispersed well in rubbery matrix, Mark proposed an *in situ* sol-gel process of tetraethoxysilane (TEOS) in the early 1980s [1]. The Latin words '*in situ*' mean 'in place', therefore, incorporating silica by means of the sol-gel reaction is considered to be a novel technique. Originally, the sol-gel process had been noted as a preparation method of inorganic glasses at low temperature [2]. The sol-gel process starts with a solution of metal alkoxide precursor and water, whereby hydrolysis and condensation reactions are employed to generate silica in the presence of an acid or a basic catalyst. The elementary reactions leading to silica formation are shown in Figure 1.1.

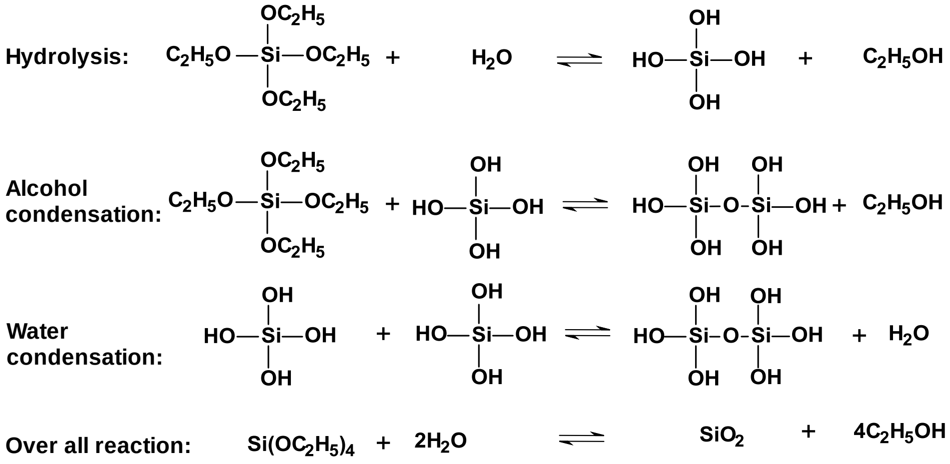

Figure 1.1 Sol-gel process: Hydrolysis and condensation reactions of TEOS.

The hydrolysis reaction replaces the alkoxide group (OC_2H_5) with a hydroxyl group (OH). Subsequent condensation reactions involving silanol groups produce siloxane bonds (Si-O-Si) plus the by-products alcohol (C_2H_5OH) or water. Under most conditions, condensation commences before hydrolysis is complete. Because water and alkoxysilanes are immiscible, a mutual solvent such as alcohol is normally used as a homogenizing agent. However, this product can be prepared without added solvent, since alcohol produced as the by-product of hydrolysis reaction is sufficient to homogenize the initial phase separate system [2]. In addition, these reactions are concurrent and demonstrate some reversibility depending on the reaction conditions, such as pH, concentration, type of catalyst and temperature. In terms of the precursor, silicon oxide is the most commonly used metal alkoxide, due to its mild reaction condition [2].

In the field of rubber science, cross-linked silicone rubber was the first rubber to be subjected to *in situ* silica filling [1]. This method has the advantage of producing homogeneously dispersed nano-silica particles in the silicone rubber matrix. The application of *in situ* silica filling has been expanded to conventional diene rubbers; for example, styrene-butadiene rubber (SBR) [3-11], acrylonitrile butadiene rubber (NBR) [12-14], and butadiene rubber (BR) [3,15,16]. Since this method was found to be useful for preparing the *in situ* silica filled diene rubbers, it was later extended to NR [17-34], including its derivatives, for example, epoxidized NR (ENR) [35,36] and grafted-NR [37-38], and so on. Thus, in 2000, this topic was summarized in a review paper [3]. Over a decade later, there are some interesting studies on the basics of *in situ* silica filling, thus the recent issues are reviewed in this chapter.

1.2 The sol-gel reaction in a swollen state of cross-linked rubber

In the early development stages of sol-gel reaction in a swollen state of cross-linked rubber matrixes, various types of cross-linked rubbers were subjected to the sol-gel reaction in order to achieve the fine dispersion of *in situ* silica. Mark and Pan [1] used silicone rubber as the first material for the swollen technique. Kohjiya *et al*. have also studied the *in situ* silica reinforcement of general-purpose diene rubbers [3-7,12-16,39]. In these cases, the reinforcement effect of *in situ* silica was considerable for rubber vulcanizates. However, the thickness of the sample was restricted for the homogeneous filling of *in situ* silica and controlling *in situ* silica content was difficult due to the limitation of swelling of TEOS in the cross-linked rubber matrix. By using this preparation technique, however, homogeneous and very fine silica particles can be introduced into the rubber matrix. For example, Ikeda *et al.* subjected peroxide cross-linked isoprene rubber (IR) to the *in situ* silica filling in order to prepare a model nanocomposite to investigate the deformation of filler in the matrix [40].

The silica content was ca. 22 phr, but the average diameter of the *in situ* silica particles was ca. 34 nm and its distribution was very narrow. The distance between the silica particles was ca. 72 nm. The sample was subjected to a simultaneous time-resolved small-angle X-ray scattering (SAXS) technique and tensile measurement. An isotropic pattern was observed before stretching, which implies that the silica particles were randomly dispersed in the rubber matrix before stretching.

By stretching the sample to $\alpha = 1.5$ and 2, the ring-shaped two-dimensional SAXS pattern was changed, where the meridional scattering increased and equatorial scattering significantly decreased. This observation suggests the formation of a buckling structure of silica particles through stretching. This morphological change of *in situ* silica particles can be ascribed to elongation in the stretching direction and compression from the lateral directions occurring simultaneously during uniaxial stretching. In addition, the four-spot pattern that identifies the buckling structure of *in situ* silica particles was clearly detected during the retracting process, which concurs with a computer simulated study on the basis of the shear displacement model by Rharbi [41-43]. The buckling structure of silica particles was clearly observed during the stretching process. In addition, good linearity was observed between the microscopic and macroscopic elongation ratio measured by the simultaneous tensile measurement, which suggests the affine deformation of the *in situ* silica filled soft nanocomposite. Therefore, this nanocomposite is presented as the most preferable model for investigating the deformation behaviour of nanofillers in soft materials.

1.3 The sol-gel reaction in a swollen state of uncross-linked rubber

As mentioned earlier, the sol-gel technique in cross-linked rubber matrixes limits the thickness of the homogeneous sol-gel reaction, and the silica content is difficult to control. In order to overcome these difficulties, an alternative practical preparation method of *in situ* silica filling in rubber was developed. This technique was introduced first by Kohjiya's group in 2001, where uncross-linked NR was swollen in TEOS to control its sol-gel reaction [17], which was found to be more practical than previous techniques because variously shaped vulcanizates can be prepared by conventional processing from *in situ* silica filled compounds. The researchers continuously investigated the morphology and physical properties of the composite in terms of the effect of silane coupling agents, i.e., γ- mercaptopropyltrimethoxysilane (γ-MPS) in the system [18]. The addition of γ-MPS to the *in situ* silica filling NR appeared to bring about more homogeneously dispersed *in situ* silica particles in the NR matrix

From their TEM results, it is clear that the *in situ* silica generated was in nanometer size, with better dispersion, compared to those of conventional mixed samples. In terms of tensile properties, composite stress was found to be improved by adding γ-MPS, which worked to increase the network-chain density of NR vulcanizates. When considering the effect of mixing techniques, i.e., *in situ* and conventional mixing, the *in situ* mix (NR-*in situ*-V) showed the higher modulus compared to the conventional mixed sample (NR-mix-V). The higher tensile strength of the *in situ* silica filled sample was achieved by a strong interaction between silica and rubber with a more homogeneous dispersion of silica in the NR matrix.

The same technique was successfully expanded to other kinds of rubber, i.e., SBR. However, generating a high content of *in situ* silica was still limited. This problem was solved by improving the swelling degree of uncross-linked rubber matrix and the type of catalysts by Ikeda *et al* [25,28]. The soaking technique was separated into two steps. Firstly, the milled rubber sheet was immersed in TEOS at 40°C for 1 h, then 25°C for 24 h. The swelling degree of the rubber sheet was dramatically increased by this technique, compared with single-step soaking. In the second step, the type and concentration of catalyst were varied and the polarity of amine was found to be important for increasing the *in situ* generation of silica in the NR matrix. The primary alkylamines with pertinent hydrocarbon segments, i.e., n-hexylamine, n-heptylamine and n-octylamine, were found to give a high content up to ca.80 phr of homogeneous *in situ* silica in NR matrix with fairly homogeneous dispersion. Furthermore, this high reactivity was obtained within ca.10 h of the reaction. The amount of *in situ* silica increased with an increased concentration of n-hexylamine. Due to its high solubility in water and TEOS, n-hexylamine was found to be the most preferable catalyst for effective *in situ* silica generation. In addition, the generated *in situ* silica was measured in nanometer-sized silica particles, as seen by the TEM photograph.

The polarity and solubility in water of primary alkyl amine were the most influential factors for controlling the *in situ* silica content in the NR matrix. The speculated mechanism of the sol-gel reaction in the swollen NR matrix was proposed. In order to reveal the characteristic of the *in situ* silica nanocomposite (NR-71Si), tensile stress-strain measurement was conducted.

As a reference, the tensile stress-strain properties of commercial silica VN-3 filled NR vulcanizate (NR-71VN) were compared. It is clear from the results that the *in situ* silica filled sample is not as stiff as the VN-3 sample, as detected by a lower modulus at elongation < 200%. The softness behaviour demonstrated in the *in situ* silica sample has been assumed to be due to the formation of smaller aggregates of silica, as seen by the TEM photograph. When stretched to greater elongation, stress of the *in situ* silica sample became higher, which can be ascribed to the higher interfacial interaction between silica and rubber matrix when compared with the VN-3 sample.

Another method to increase *in situ* silica content was reported by Poompradup *et al* [31,32],who focused mainly on the effect of solvent. They found that tetrahydofuran (THF) was the most suitable solvent for the sol-gel reaction, compared with chloroform and carbon tetrachloride which have much lower polarity than THF, which is not favourable for penetration of silanol reagent and water during hydrolysis and condensation reactions. However, in this study, under optimum conditions the *in situ* silica content generated was up to 70 phr, which is comparable to that of the solvent-free system reported by Ikeda *et al*. It may be concluded that a utilization of the solvent-free system in the sol-gel reaction is more practical.

With developments in the preparation method of the sol-gel reaction of TEOS in rubber, characterization also progresses. In particular, morphology of the nanocomposites has been investigated three-dimensionally in nano scale, and conventional TEM has proved a powerful tool in virtualizing the morphology of filler in rubber networks. However, the conventional TEM projects a three-dimensional (3D) body on to a two-dimensional (2D) (x,y) plane, hence the structural information on the thickness direction (z-axis) is only obtained accumulatively. This lack of z-axis structure poses tricky problems in estimating 3D structure in the sample, resulting in fairly misleading interpretations. By combining TEM and computerized tomography techniques, the 3D-TEM technique has been established to afford 3D structural images, which are known as ‘electron-tomography’ [29]. The 3D-TEM technique was introduced into the field of rubber technology in 2004 by Kohjiya *et al* [22] and his group investigated the relationship between the three-dimensional morphology of filler and physical properties of rubber materials [22-24,29]. The *in situ* silica nanocomposite was the first sample subjected to the 3D-TEM analysis.

The 3D-images were reconstructed by using two-dimensional 66 slice TEM images. Neighbouring particles or aggregates are shown in different colours to make the silica dispersion easier to see. As seen from the images, a few silica particles are in contact with each other to form an aggregate both of conventional (VN) silica and *in situ* silica. The *in situ* silica had a larger primary particle radius than the VN-3 silica, and the radius showed less homogeneity. Furthermore, the aspect ratio of the silica aggregates was also calculated using the minimum and maximum length determined in 3D-TEM images for all silica particles and aggregates. The results are plotted in Fig. 1.10 (b), and it was found that the *in situ* silica is less symmetric in shape than the conventional silica. Since *in situ* silica is produced and grows in the un-crosslinked NR matrix by the sol-gel reaction of TEOS, the shape of generated silica particles is liable to become non-symmetrical. On the basis of a series of comparative measurements of physical properties, it was concluded that the *in situ* silica had a lower surface concentration of silanol groups than the VN-3 silica. As a result, the interaction between silica and rubber was stronger for *in situ* silica than VN-3 silica, which presumably affected the homogeneity in the size of the silica aggregates [24].

The synthesis of *in situ* silica in swollen rubber matrixes before the cross-linking reaction has been proclaimed as a powerful technique to generate a high silica content in rubber matrix. From morphological analysis it can be concluded that this technique provides a homogeneous dispersion of particulate silica, which consequently promotes tensile behaviour of the nanocomposite. Therefore, many researchers have recently presented studies that use this technique with other kind of rubbers, according to their specialty. The focus is then on extending this technique on to an industrial scale, and investigating the specific properties for replacing some carbon black products.

1.4 Silica generated *in situ* in synthetic rubber latex

After the pioneering study made by Mark's group in the early 1980s, and further developed works by many researchers as reviewed in the previous section, another method of the sol-gel reaction was reported in 1996 by Yoshikai's group [8]. In their study, the sol-gel reaction of TEOS was conducted in rubber latex in order to improve the interpenetration of inorganic filler into rubber matrix compared with the *in situ* silica filling using swollen rubber matrixes. In their work, the *in situ* silica/rubber composites were prepared by mixing SBR latex, TEOS, water, and NH_3 as a catalyst together at room temperature, then heating the mixture at 40^oC for 24 h. The obtained compound was dried and subjected to conventional mixing and pressing at 150°C. It was reported that the amount of TEOS and the molar ratio of water to TEOS ($[H_2O]/[TEOS]$) were related to silica content and particle size, respectively. Under optimal reaction conditions, where an over 90% conversion of TEOS to *in situ* silica was achieved, 44 wt % of *in situ* silica was obtained; however, the diameters of the silica particles were larger than 100 nm. Excellent tensile properties were observed when the *in situ* silica content was increased. The study was extended into NBR latex and a similar result to those of SBR latex was reported, where the maximum amount of generated *in situ* silica was ca. 40 wt %. It was noted that the amount of generated silica was limited by the latex destabilizing after the addition of TEOS [9].

1.5 *In situ* silica generation in NR latex

Following the studies into generating *in situ* silica in synthetic rubber latexes, utilization of NR latex for the sol-gel reaction was reported by Toutorski *et al* [10,11]. However, in their case, other types of precursor, i.e., sodium-zinc-silicate, was used in NR latex. The reaction condition was also preceded at room temperature. In their study, the presence of ZnO acetate in the precursor was clearly found to improve tensile strength of the composites even in the curing system where ZnO was not included. However, sodium-zinc-silicate as a precursor could not be used extensively for this reaction because the utilization of TEOS had already been established as one of the most effective precursors for the sol-gel reaction by swollen technique.

Tangpasuthadol *et al.* then reported a study on generation of *in situ* silica in NR latex by using TEOS as a precursor [30], in which they presented the advantages of using commercial grade NR latex, i.e. high ammonium (HA), which contained 0.7 wt % NH_3 for the reaction. Since commercial grades of NR latex generally use NH_3 as a main preservative, they expected that NH_3 could function as a catalyst when the latex is employed in sol-gel reaction. Thus, in their experiment, NR latex was directly mixed with TEOS without an additional basic catalyst. The mixture was then subjected to the sol-gel reaction at 50°C for five days. Successful conversion of TEOS into *in situ* silica was very high, over 90%. However, they reported that the highest *in situ* silica content in their samples was limited to ca.19 phr. This limitation was explained by the destabilization of NR latex when a high amount of TEOS was added; for example, when 70 phr of TEOS was added into the latex, they detected some phase separation. After the generation of the *in situ* silica in NR matrix, the composite was subjected to the two-roll milling and cross-linking process by heat-pressing. This study focused on the effect of TESPT on the mechanical and morphological properties of the composite. TESPT was found to improve both mechanical and morphological properties of the composite as expected. In terms of morphological properties observed by SEM, however, the average diameter of *in situ* silica particles was found to be quite large, i.e., estimated to be nearly 500 nm.

TEOS is a typical precursor for *in situ* silica formation and gives a high conversion in NR latex. Therefore, Tangpasuthadol's group conducted the same reaction in NR latex using difference precursors [33], i.e., vinyl triethoxysilane (VTOS), ethyl triethoxysilane (ETOS), and *iso*-butyl triethoxysilane (BTOS). Their chemical structures. They reported that the silane conversion to silica in the NR matrix was almost complete for TEOS, but it decreased when the alkyl group of the alkyltriethoxysilane increased in size. These results were explained in terms of the structure and polarity of the silanes.

The TEOS molecule contains four ethoxy groups, and therefore undergoing hydrolysis and condensation to form silica almost completely resulted in the highest per cent conversion to silica. The other three alkyltriethoxysilanes – VTOS, ETOS, and BTOS – on the other hand, contain one alkyl substituent connected to the silicon atom. The iso-butyl group in BTOS is very bulky and therefore partially inhibits the hydrolysis and condensation reaction during the sol-gel process. The mixed TEOS-BTOS sample formed low molecular weight resin and tended towards phase separation of the polar medium due to the low polarity of the butyl group. ETOS and VTOS are of similar sizes, but the vinyl group is more polarized than the ethyl. VTOS should be more compatible with the polar medium and thus more reactive during the sol-gel process in the rubber matrix than the ETOS. In terms of morphological characteristics, alkylated silica particles of a size under 100 nm were found to be well dispersed in the NR matrix, unrelated to the type of silane.

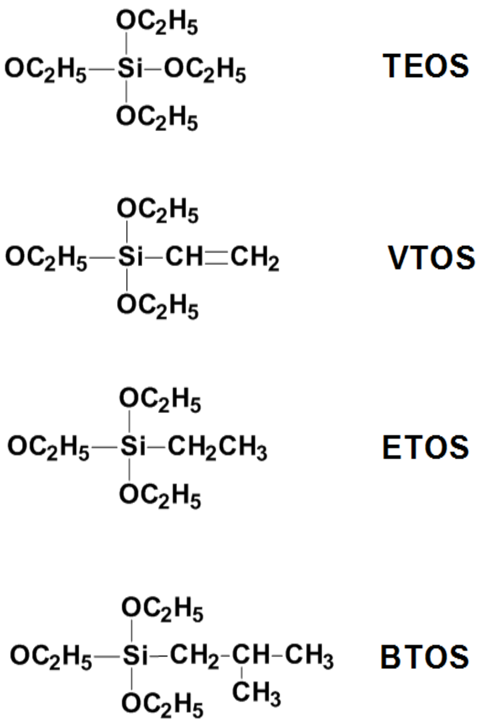

Figure1.12 Chemical structures of four alkoxysilanes: tetraethoxysilane (TEOS), vinyltriethoxysilane (VTOS), ethyltriethoxysilane (ETOS), and iso-butyltriethoxysilane (BTOS).

The sol-gel reaction of tetraethoxysilane in NRlatex was conducted to produce *in situ* silica-filled NR latex, followed by adding sulfur cross-linking reagents to the latex in a liquid state. The latex was cast and subjected to sulfur curing to result in a unique morphology in the NR composite of a flexible film form. The contents of *in situ* silica filling were controlled up to 35 phr. It was also found that not only the amount of TEOS but also the concentration of rubber in the latex are important to control the generation of *in situ* silica, especially to increase the silica content in the composites by using liquid state preparation method.

Therefore, the dilution of NR latex was useful in decreasing the concentration of rubber colloid particles and resulted in less aggregation among the rubber and generated silica colloids. In general, the silanol group is well known to be acidic. Thus, a strong base, such as an amine, may deprotonate the silanol groups to form a negatively charged silica surface and quaternary ammonium ions in the solution [2]. NR particles in the latex containing NH_4OH, on the other hand, were reported to be covered with negatively charged fatty acid [44]. Therefore, the control of concentration of negatively charged colloid particles in the latex must be key for stabilizing the NR latex, and consequently, for increasing the *in situ* silica content in the composites.

The *in situ* silica filling and sulfur cross-linking being reflected on the latex state gave a new type of NR composite, which was prepared by taking advantage of the liquid state of the NR latex [46,47]. The addition of sulfur cross-linking reagents in a liquid state without any coagulation was a key for preparing the composites with 10, 19, and 35 phr of the silica content. The sol-gel reaction of TEOS occurred in the water phase not inside the rubber particles in the NR latex, which resulted in a characteristic morphology composed of silica around rubber particles. The silanol groups on the *in situ* silica is supposed to absorb some of the added sulfur in the latex, and consequently, the amount of sulfur used in the sulfur cross-linking reaction decreased with increasing silica content.

1.6 Applications of *in situ* silica

By the development on *in situ* silica generation in the rubber matrixes and rubber latexes, not only the size and content but also the morphology of *in situ* silica particles is suggested to be controlled when specific reaction conditions are organized. Therefore, the application of *in situ* silica will be expanded to many rubber products. For examples, the biphasic structured *in situ* silica filled NR composite may be useful as a sealing product for gases and liquids. The softness of *in situ* silica filled NR may be preferable for application to biomedical materials. High performance NR materials are expected to play an important role to maintain the sustainable society on the Earth.

1.7 Conclusions

For preparations of high performance *in situ* silica filled NR nanocomposites, the authors emphasize a few key issues on the *in situ* silica filling in NR. On the swollen technique, it is important at first to control the amount of alkoxysilane precursor in NR in order to obtain the desired silica content. A kind of catalyst is also a key to control the *in situ* generated silica content and size in the NR matrix. Therefore, some specific reaction conditions may be further developed in order to improve the properties of NR nanocomposites. On the latex method of *in situ* silica filling, on the other hand, the stability of latex during the *in situ* sol-gel reaction of alkoxysilane will be improved in order to increase the content and to decrease the size of generated silica particles. Adequate stabilizers may be searched for further development the sol-gel reactions.

Applications of *in situ* silica filling for high functionality rubber materials will be studied both from academic and industrial viewpoints. Well-dispersed nono-sized silica particles and selectively formed silica networks in the NR matrix must be useful to produce new NR composites for constructing a safe and eco-friendly world in the 21 century.

NR is originally a high performance rubber material. Therefore, it is necessary to keep the advantages of NR itself for material designs of NR composites. As shown in our template preparation method of *in situ* silica using rubber particles in NR latex, a utilization of non-rubber component in NR may be one of the keys in further improving the properties of NR materials.

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CHAPTER 2

Chapter 2

Characterization of biphasic-structured soft composite prepared from *in situ* silica filled natural rubber latex

Natural rubber (NR) is an indispensable material in our society. NR based soft composites have been regarded as one of the most successful materials for industrial products among many polymer composites [1-2]. Composite from *in situ* silica filling in NR latex is of interested in this study. As mentioned in the General Introduction, *in situ* silica generated in NR latex and processed through liquid-state mixing is expected to have an advantage in the better dispersion compared to other techniques. However, preparation of the composite in liquid state is more difficult than the solid state due to destabilization of NR latex, thus the generated content of *in situ* silica in the latex was relatively low [3-5]. The study on preparation of *in situ* silica filling NR latex was carried out previously [6]. In the previous work, preparation technique to obtain high content of *in situ* silica generated in NR latex and further mixed with sulfur cross-linking reagents in liquid state was established [6]. In addition, the composite mixtures were subjected to a film-forming process in order to retain a fine dispersion of *in situ* silica in NR matrix which supposed to bring about good mechanical properties [6]. In the previous work, however, a clear conclusion on the relationship between morphology and mechanical properties could not be drawn due to the lack of information on its morphological result.

Therefore, in this study, further study on relationship between morphology and mechanical properties of the composite was investigated, especially, mechanism of the formation of situ silica in NR latex was aimed to disclose. A few evidences which introduced in this study, e.g., Transmission electron microscopy (TEM) photographs, X-ray absorption near-edge structure (XANES) spectroscopy spectra [6] and composition of the composite latex brought us a clear image to have a conclusion on the formation of the composite film. The composite was further subjected to a dynamic mechanical analysis (DMA) in order to investigate a relationship between the formation of situ silica in rubber latex and dynamic mechanical properties. Finally, understanding in the mechanism of film formation to have a specific morphology will be of use in development of new high performance material which produced from the sustainable resources.

By the TEM observation, the specific morphology of *in situ* silica was observed. By joining the XANES results, mechanism in forming of the unique structure is proposed in this Chapter. It can be speculated that the sol-gel reaction of TEOS occurred in the water phase not inside rubber particles in NR latex, which resulted in a characteristic morphology composed of silica around rubber particles. The silanol groups on the *in situ* silica is supposed to absorb some of the added sulfur in the latex and consequently the amount of sulfur used in the sulfur cross-linking reaction decreased with increasing the silica content. As the results, the fraction of short polysulfidic linkage in the polysulfidic one increased in the cross-linked NR composites. The *in situ* silica filling in NR latex clearly showed a good reinforcement effect. With the increase of silica content, the reinforcement effect became larger in agreement with a general phenomenon of reinforcing filler. However, the locally dispersed *in situ* silica filling in this study resulted in the unique dynamic mechanical properties. This new preparation method for *in situ* silica filled composites may be of use for a material design of functional rubber products. The present observations will give a new concept for developing the applications of composites prepared from NR latex.

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CHAPTER 3

Chapter 3

Strain-induced crystallization of biphasic-structured soft composites prepared from natural rubber latex and silica generated in situ

Natural rubber (NR) has been widely recognized as a useful soft mater, which is both highly elastic and crystallizable under high strains [1-3]. NR is indispensable for manufacturing pneumatic tires of heavy-duty uses *e.g.* those for aircrafts, heavy trucks and rubber bearings in a seismic isolation system [1-4]. Thin NR films, which are directly prepared from NR latex without coagulation, are also very important materials for biomedical and health care fields [1,5,6]. These extensive applications of NR are based on its high elasticity and excellent mechanical strength. The latter is ultimately attributable to its ability of crystallization upon stretching [1-4,7-11]. Therefore, it is necessary to evaluate the strain-induced crystallization (SIC) behavior for development of high performance NR materials.

Up to now, the SIC behavior of NR have been extensively studied [7-20]. The research group of one of the authors has also carried out studies on the SIC not only for cross-linked NR [16-19] but also for filler-filled cross-linked NR [21-23]. A general tendency of the SIC behavior of NR was thus established [16-19]: Upon tensile deformation, polymer chains start to be stretched. Among the polymer chains, short ones are fully-stretched first, and these fully-stretched chains can act as precursors for crystallization like a nucleus of crystallites. Therefore, the NR crystallites are usually observed to grow up in the direction perpendicular to the molecular chain axis [22,23]. Upon stretching, the generation of crystallite is generally found to be linearly increased in cross-linked NR samples. Since the distribution of network chain length is not mono-dispersed, the SIC behavior depends on the heterogeneity of cross-linked rubber [19,24], which is significantly related with cross-linking systems such as sulfur or peroxide cross-links. In addition, the non-uniformity of NR also affects the SIC due to the presence of non-rubber components, as it was proved by atomic force microscopy and small-angle neutron scattering analyses [25,26].

Reinforcing fillers, on the other hand, have been known to be of remarkable influence on the SIC of NR because of their strong interfacial interactions with the polymer matrix. Studies on the SIC behavior of carbon black/NR composites have been especially focused due to the importance for heavy-duty uses [21,22,27-30]. Among these studies, there are some common observations: By the inclusion of carbon black, a start of SIC shifted to a lower strain, *i.e.*, the SIC was apparently accelerated. This tendency was, however at least partially explained due to the decrease of volume fraction of NR in the material by the isotropic filler inclusion. In terms of crystallinity, it was commonly observed to linearly increase with an increase of strain similarly with non-filled NR. These phenomena were also detected in commercial silica filled NR-based composites [29] and *in situ* silica filled one [23].

Recently, we prepared novel biphasic structured *in situ* silica filled NR composites by a sol-gel reaction of tetraethoxysilane using *n*-butylamine in NR latex [31]. This preparation procedure is a kind of soft process as the composites were prepared by liquid-state mixing and followed by casting to obtain thin films. In the composites, the *in situ* silica was locally dispersed around rubber particles to result in the specific morphology. Namely, NR particles in the latex worked as templates to form the novel biphasic structure in the composites. The rubber phase in the biphasic structure was of higher purity than that of the composite prepared by conventional mechanical mixing. Thus, unique dynamic mechanical properties were detected in the composites. In order to further clarify the characteristics of the biphasic structured *in situ* silica filled NR composites, the simultaneous synchrotron wide-angle X-ray diffraction (WAXD) and tensile measurements were conducted in this study. Nowadays, *in situ* generated silica in a rubbery matrix moves forward into the nano-technology [32-34]. Therefore, present results will be useful for further developing of rubber-based nano-composites.

The time-resolved WAXD measurement during stretching revealed that the SIC of the biphasic structured *in situ* silica filled NR soft composites occurred stepwise, i.e., the degree of crystallinity showed the repetition of increase and standstill cycles. This behaviour was found on the composites prepared from NR latex with *in situ* silica by using the liquid-state mixing and casting methods. The unfilled NR latex vulcanizate prepared by casting also showed the stepwise SIC, although the steps became obscured with the increase of strain. The presence of new biphasic structure in the NR latex vulcanizate brought about the increase of oriented amorphous chains to result in the promotion of SIC, where the generation of small crystallites dominantly occurred stepwise due to the silica phases around the rubber phases. The small crystallites worked as nano-fillers to reinforce NR *via* the oriented amorphous chains. Since the *in situ* silica was not introduced inside the rubber phases but on the surface, the observed characteristic phenomena of the SIC may be of interest in understanding a role of filler network for the reinforcement of rubber. The role has been one of the big questions in rubber science and technology, because the ideal model composite only with filler networks has been difficult to be prepared. For further development of rubber science, a study on the biphasic structured NR composites with different silica contents will be necessary from the viewpoints of silica contents and cyclic deformation, which will be reported in a near future.

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CHAPTER 4

Chapter 4

Role of *in situ* silica network on strain-induced crystallization of natural rubber revealed by cyclic tensile deformation

It is well-known that in reinforcement system, where particulate nanofiller was mixed into rubber matrix, surface of the filler particles is covered by the rubber layer, called as bound rubber, filler gel, or immobilized layer [1-4]. Due to the interaction between particle surfaces, nanoparticles are supposed basically to be present as aggregates. The filler aggregates in the polymer matrix have a tendency to associate into agglomerates, especially at high loading, leading to network-like structures or clusters.

In case of carbon black, once it was mixed into rubbery matrix at sufficiently high loading, it has been assumed that agglomerates can be formed into filler network structure [1-5]. This filler network has been thought to explain specific mechanical properties such as Payne effect [6-8] and Mullins effect [9]. Many rubber technologists assume that the networks formed by carbon black in the rubbery matrix are one of the important factors for rubber reinforcement by carbon black. As a result, it has been a target of rubber technologists for many years to demonstrate an intrinsic role of filler network.

In facts, a preparation of filler network model is known to be very difficult. So far, conventional processing technique was used to prepare composite which requires sufficiently high filler loading to form the network. However, a clear network structure, clear boundary between filler network and rubber matrix could not be achieved. As various kinds of filler structure can be formed by the mechanical mixing. Not only in the case of carbon was black but particulate silica also subjected to prepare the filler network structure in rubber matrix [10]. By utilizing 3D TEM analysis, various levels of silica structures, for example, so-called isolated chains are found to be formed in the nanocomposites [10].

Therefore, in this Chapter, the *in situ* silica filled uncross-linked composite which presented in the previous Chapters is utilized as a model of filler network. The *in situ* silica/natural rubber composite is supposed to be one of the most suitable models for evaluating the effect of filler network on strain-induced crystallization (SIC) of NR matrix. Even it contains *in situ* silica only 10 parts per hundred of rubber, but the formation of filler network is obviously detected [11,12]. The formation of *in situ* silica network is ascribed to the preparation technique, i.e., soft processing technique [11]. Previously in Chapter 3, the *in situ* silica network already detected to affect on strain-induced crystallization (SIC) behavior of natural rubber (NR). Depend on deformation scale of the composite, SIC behavior of the NR was found to be significantly affected [12]. However, it was difficult to separate the effect of SIC and cross-linking on the SIC behavior.

Therefore, in this Chapter, the author aimed to verify the role of *in situ* silica network on strain-induced crystallization behavior under cyclic deformation of natural rubber. The obtained results are believed to be the basic criteria for material design of nanocomposites.

Role of *in situ* silica network on strain-induced crystallization of natural rubber is elucidated in this Chapter. It was demonstrated that filler network of *in situ* silica has strong interaction of both filler-filler and filler-rubber. Especially, the filler-filler interaction was first reported in this study that it was resulted in high oriented amorphous index (*OAI*) which further resulted in this tensile stress. The filler-rubber interaction, on the other hand, seems to work to maintain the SIC behavior and thus tensile properties of the composite since it contains no chemical cross-linking sites. Thus, it may suggest that, filler network contains two different features, i.e., filler-filler and filler-rubber interactions in bringing a high reinforcement to the composite in particular ways. Therefore, not only filler-rubber interaction but also filler-filler interaction that composts in the filler network is also a key to control mechanical properties of the composite.

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CHAPTER 5

Chapter 5

Peroxide cross-linked soft composite prepared from natural rubber latex and silica generated *in situ*

Recently, *in situ* silica generated in natural rubber (NR) latex is being focused among rubber scientists as it is expected to provide a fine dispersion of *in situ* silica in rubber matrix [1-9]. Previously, the biphasic structure of *in situ* silica/NR composite was reported. The biphasic-structured composite can be achieved by conducting the sol-gel reaction directly into rubber latex, for example, natural rubber (NR) latex, followed by film-casting process [10]. Moreover, the biphasic-structured composite was found to show a unique strain-induced crystallization (SIC), i.e., stepwise SIC [12]. The stepwise SIC was observed as the composite contains difference size of *in situ* silica network structures [11]. Additionally, strong filler-rubber interaction was detected in the biphasic-structured composite as evidence by SIC behavior under cyclic tensile deformation as shown in the Chapter 4. The strong filler-rubber interaction was explained to be generated during the film forming process under the presence of quaternary ammonium ions that works to chemically linked between *in situ* silica particles and rubber particles as discussed in Chapter 1. Therefore, this technique is believed to be useful for preparation of high performance rubber products.

It was however noticed that, in some applications, the compound must be subjected to mix with variety of ingredients in order to achieve any desire properties. Such a mixing process is usually done by mechanical milling. In this Chapter, therefore, the biphasic-structured composite which contains 10 parts per hundreds of rubber (phr) was subjected to mix with cross-linking reagent on a two-roll mill and carry out the cross-linking reaction by heat-pressing process. Thus, it can be speculated that, biphasic structure which formed in the composite can be broken down by these processes. The change in morphology of composite after mixing process is followed by transmission electron microscope (TEM). Afterward, mechanical properties of the composite are compared with that of original sample. Furthermore, by conducting SIC study, information on filler-rubber interaction can be disclosed.

In this Chapter, it is noted that, differently from the previous Chapters, peroxide cross-linking system was used in order to make the system simpler than that of sulfur system. Finally, relationship between mechanical properties and morphology of the composite will be discussed comparatively with that of original composite.

The time-resolved WAXD and tensile measurement revealed that *in situ* silica generated in rubber matrix found to be perturbed the SIC behavior of NR matrix. The perturbation of SIC can be ascribable to a strong interfacial interaction between *in situ* silica and rubber matrix. The strong interfacial interaction is more pronounced when the composite was subjected to dynamic mechanical analysis as it showed much higher storage modulus and lower tan δ_{max} than that of unfilled sample. It should also be noted that formation of aggregate structure in the composite leads to the faster softening of composite comparing with the unfilled one when the temperature is higher than 75^{o}C. However, this problem may minimize in the more rigid system, i.e., higher cross-linking density or higher amount of filler. Therefore, in this study, an origin of tensile properties of the composite can be clarified to be mainly due to the reinforcement effect of *in situ* silica. For further understanding in this area, a study on the composites with has higher silica contents will be necessary and also a tensile cyclic deformation will be useful to further investigate role of Mullins effect on SIC behavior.

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SUMMARY

The novel biphasic-structured composites prepared by in situ silica filling in natural rubber (NR) latex were characterized through this study. Chapter 1, delivered as a basic understanding on sol-gel reaction in NR which has a large variety in processing technique. However, in this study, liquid-state processed composites were focused as it was expected to reveal an intrinsic morphological feature of in situ silica that was synthesized in NR latex. In Chapter 2, by TEM analysis, a unique morphology of the composite was observed, i.e., in situ silica was found to be locally dispersed around rubber particles. That is to say, NR particles work as a template for the formation of biphasic structure. Thus, according to the evidences from TEM results and surface chemistry of substances in the system, a mechanism of film-formation of the biphasic structured composite is proposed in this study. The biphasic structure which contains of pure rubber phase and silica network phase is the new finding in reinforcing natural rubber (NR) with silica. The biphasic structure has an advantage not only reinforced rubber in dynamic deformation but also a high impact resistance due to the pure rubber phase can be responsible for high energy dissipation.

In Chapter 3, an advantage of the forming biphasic structure is more announced as revealed by SIC analysis. Simultaneous time-resolved wide-angle X-ray diffraction and tensile measurement revealed the relationship between characteristics of the biphasic structure and tensile stress-strain properties associated with SIC. The results showed a stepwise SIC behavior of NR-based composites for the first time. The pure rubber phase in the biphasic structure was found to afford highly oriented amorphous contents together with oriented crystallites. The generated crystallites in the composites, whose lateral crystallite size was smaller than that of unfilled sample, were estimated to work as a reinforcing filler to result in high tensile stresses of the composites. In addition, it was also estimated that the biphasic structure of in situ silica is a kind of filler network. In order to clarify this point, the uncross-linked composite was subjected to simultaneous cyclic tensile and WAXD analyses as presented in Chapter 4. It was demonstrated that filler network of *in situ* silica has strong interaction of both filler-filler and filler-rubber. Especially, the filler-filler

interaction was first reported in this study that it was resulted in high oriented amorphous index which further resulted in high tensile stress. The filler-rubber interaction, on the other hand, seems to work to maintain the SIC behavior and thus tensile properties of the composite since it contains no chemical cross-linking sites. Thus, it may suggest that, filler network contains two different features, i.e., filler-filler and filler-rubber interactions in bringing a high reinforcement to the composite in particular ways. Therefore, not only filler-rubber interaction but also filler-filler interaction that composts in the filler network is also a key to control mechanical properties of the composite.

The effect of filler-rubber interaction became much clearer when the composite was subjected to milling process as presented in Chapter 5. By subjecting the composite to milling process, the broken down of filler network is clearly detected by TEM image. However, in term of SIC results, it was noticed that *in situ* silica generated in rubber matrix found to be perturbed the SIC behavior of NR matrix. The perturbation of SIC can be ascribable to a strong interfacial interaction between *in situ* silica and rubber matrix. The strong interfacial interaction is more pronounced when the composite was subjected to dynamic mechanical analysis as it showed much higher storage modulus and lower tan δ_{max} than that of unfilled sample. Therefore, in this Chapter, an origin of tensile properties of the composite can be clarified to be mainly due to the reinforcement effect of *in situ* silica.

In this study, not only an advantage of the liquid-state mixing technique to obtain the biphasic structured composite is enclosed but also the unfilled one which showed an excellence tensile properties. Therefore, the author also aimed to emphasize an advantage in utilizing NR latex as a starting material and process through the solution state. Many functional materials, especially for biomedical usage, NR latex is now well known to serve this area. Therefore, this study can be useful for development of high performance material.

Thus, from these five Chapters, the characteristic of composite was revealed as a new high performance material for rubber applications. The biphasic structured composite development through the studies can be useful for the further preparation of a specific structured composite material. However, the author may suggest that, further investigation of the composite which contains higher content of in situ silica. In addition, the details analysis on rheology behavior would be useful for the development of the composite.

LIST OF PUBLICATIONS

1. A.Tohsan and Y. Ikeda, “Generating particulate silica fillers *in situ* to improve the mechanical properties of natural rubber” Accepted to be published in “Chemistry, manufacture and applications of natural rubber” S. Kohjiya and Y. Ikeda, Eds, Woodhead Publishing, Oxford. (Chapter 1)

2. Atitaya Tohsan, Pranee Phinyocheep, Sumet Kittipoom, Wanwisa Pattanasiriwisawa and Yuko Ikeda, “Novel biphasic structured composite prepared by *in situ* silica filling in natural rubber latex” Polymers for Advanced Technologies, Vol. 23, pages 1335–1342, (2012) (Chapter 2)

3. Yuko Ikeda, Atitaya Tohsan, “Stepwise strain-induced crystallization of biphasic-structured soft composites prepared from natural rubber latex and silica generated *in situ*” Submitted to Colloid and Polymer Science for publication (Chapter 3)

4. Yuko Ikeda and Atitaya Tohsan, “Role of *in situ* silica network on strain-induced crystallization of natural rubber revealed by cyclic tensile deformation”, In preparation to be submitted to an academic journal (Chapter 4)

5. トーサン アチタヤ，ピンヨチープ プラニー， 浦川 宏，池田裕子（*Atitaya Tohsan, Pranee Phinyocheep, Hiroshi Urakawa, and Yuko Ikeda*）, “天然ゴムラテックスと *in situ* シリカから作るパーオキサイド架橋ソフトコンポジット Peroxide Cross-linked Soft Composite Prepared from Natural Rubber Latex and Silica Generated *in situ*）”，繊維学会誌，印刷中
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